THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVII OCTOBER 1952 No. 10

CONTENTS:

Secretary's Notice - - - - - - - - - - - 633

Collagen Purity as Measured by Ultraviolet Spectrophotometry *By* IRWIN W. SIZER - - - 634

Treatment of Leather with Polyisobutylene *By* RENE OEHLER, SVERRE DAHL and T. J. KILDUFF - 642

Note on the Isoelectric Point of Chrome Tanned Collagen *By* S. G. SHUTTLEWORTH - - - - - - 660

Abstracts - - - - - - - - - - - - - - - 664

SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
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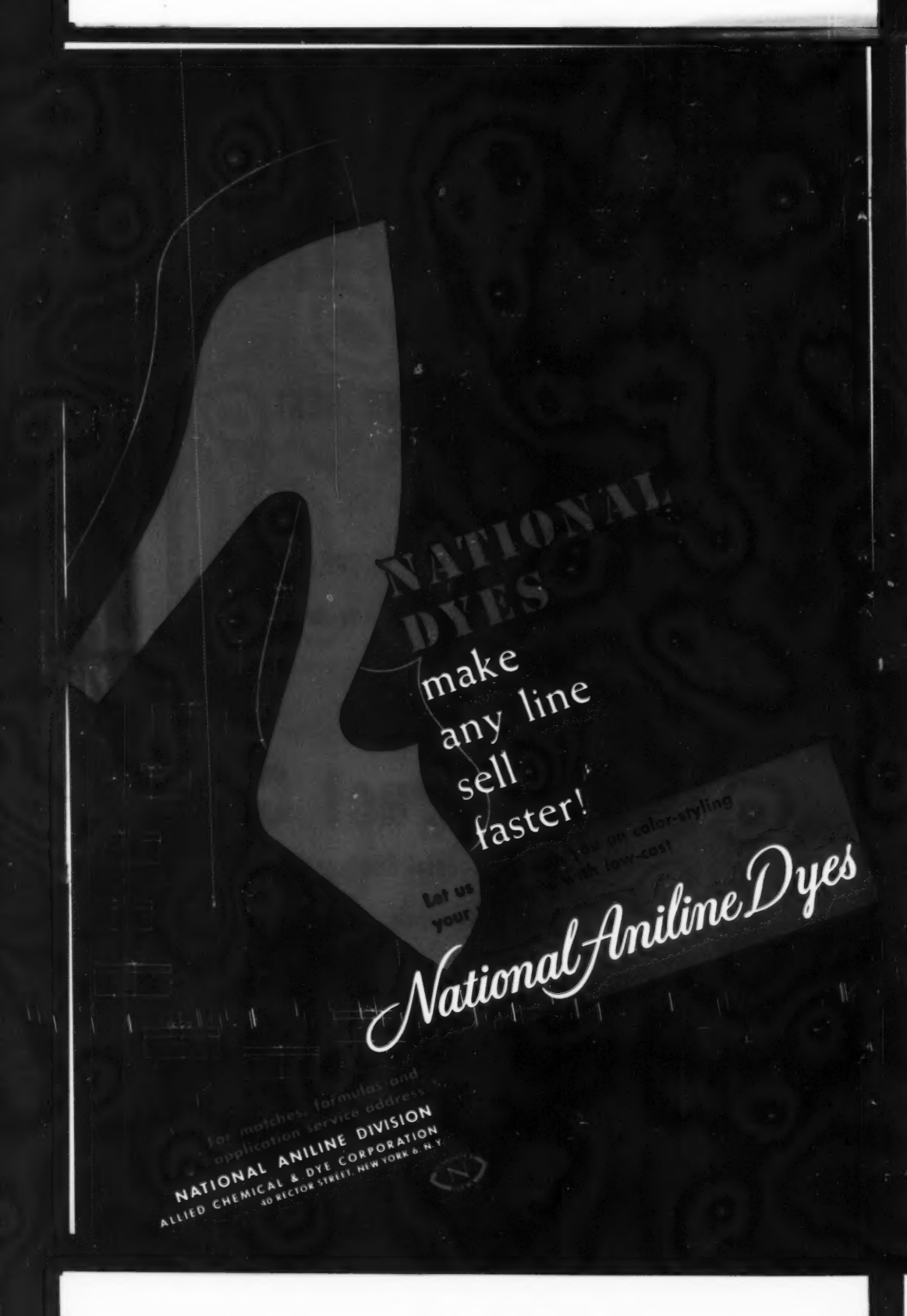
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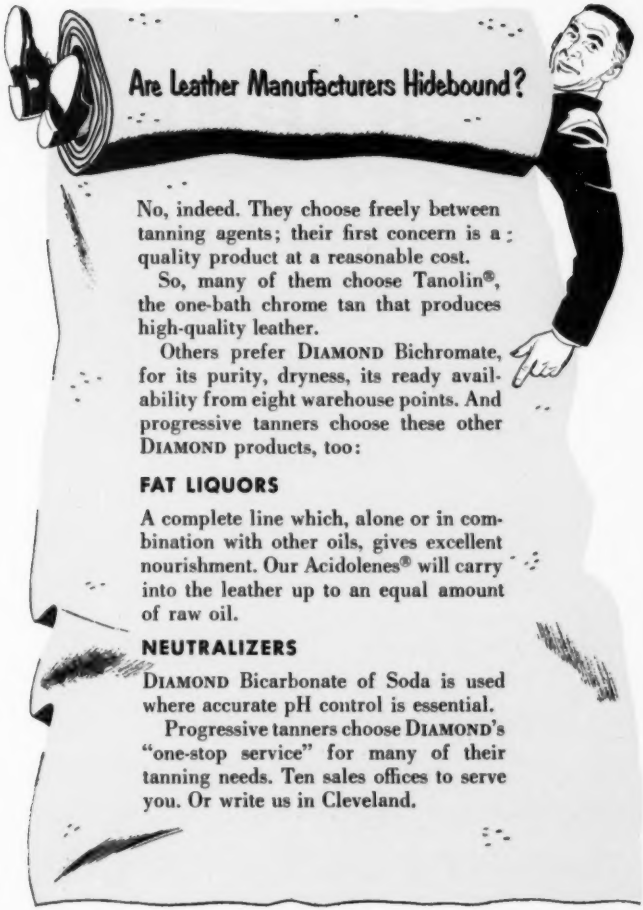
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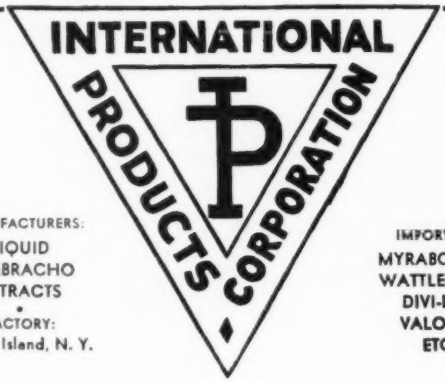

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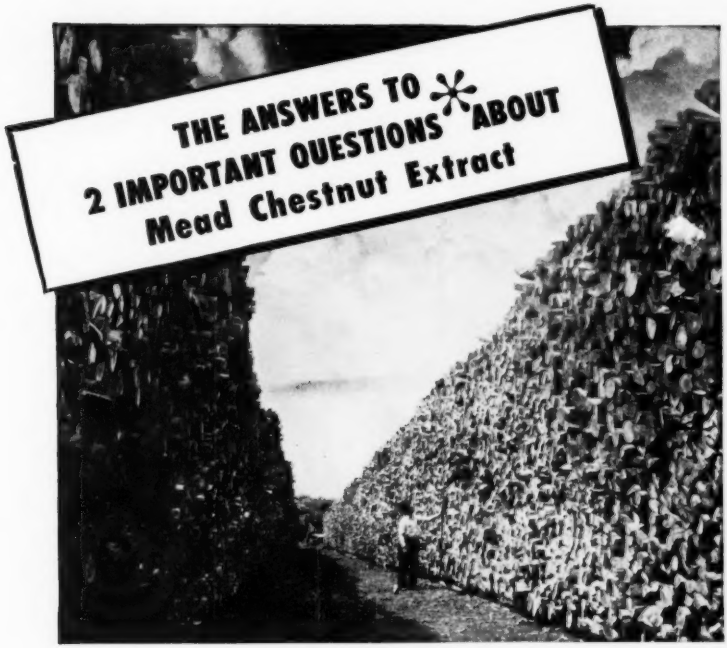

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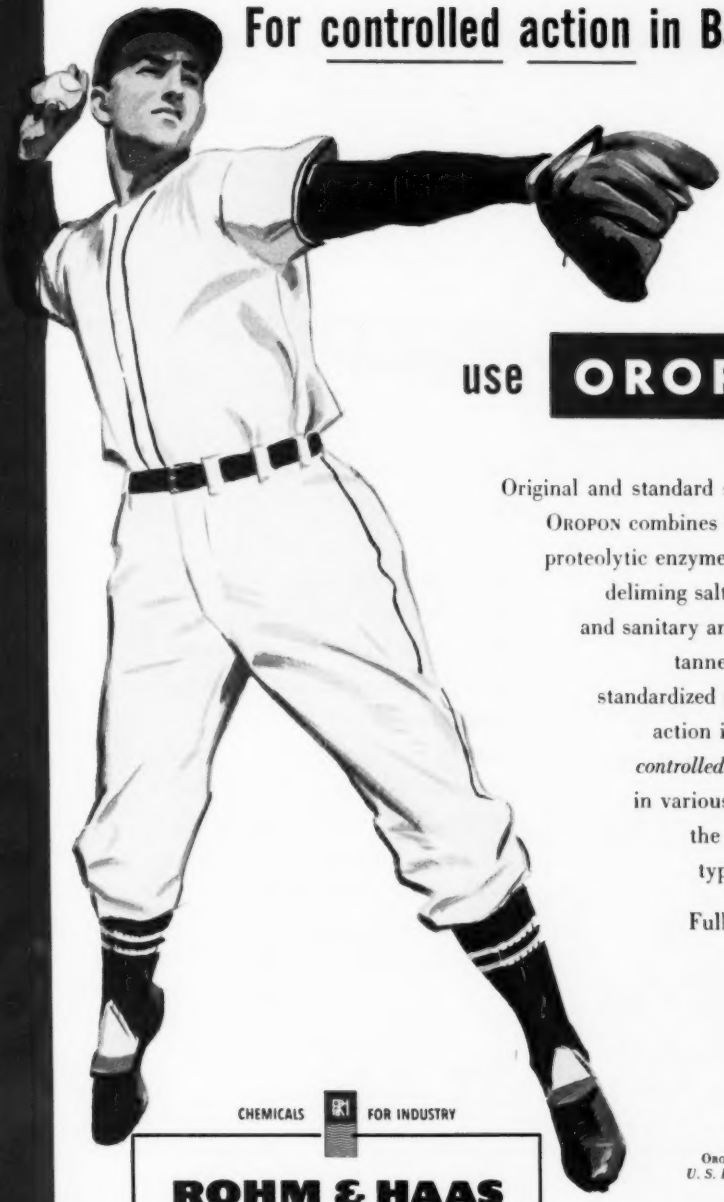

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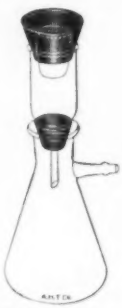

Fig. 2, showing Size 5 Adapter in use supporting a 25 ml Gooch Crucible in Filter Tube which, in turn, is supported by Size 3 Adapter in the neck of a 500 ml Filter Flask.

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Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

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Collagen Purity as Measured by Ultraviolet Spectrophotometry*

IRWIN W. SIZER†

Department of Biology
Massachusetts Institute of Technology
Cambridge, Massachusetts

Information concerning the purity of collagen preparations has been obtained from a variety of techniques such as electron microscopy [1], X-ray diffraction [2], amino acid analysis [3], and more recently from ultraviolet spectroscopy [4]. The last method is based on the fact that purified collagen contains very little of the aromatic amino acids, tyrosine, tryptophane and phenylalanine, which largely account for the ultraviolet absorption of proteins in the region from 270–290 mμ. Loofbourow et al. [4] used as a criterion of collagen purity the ratio of the minimum in absorption at about 260 mμ to the maximum at about 280 mμ. This ratio was found to increase as the collagen was progressively purified. In their study homogenates of collagen in 5 per cent acetic acid were examined spectroscopically either as suspensions or dried out in the form of transparent films. The films of collagen seemed to yield absorption spectra qualitatively similar to those of the solutions of collagen.

The present investigation involves a further study of the ultraviolet absorption spectrum of native collagen in the form of films and of collagen hydrolysates in solution and attempts to evaluate the spectrum as a quantitative measure of collagen purity. The evaluation of purity by spectroscopic methods is compared with the index of purity obtained from tyrosine analysis of collagenous preparations.

Materials and Methods

A variety of collagenous materials has been used in this study including beef Achilles' tendon, kangaroo tail tendon, crude sheep intestine, crude sheep serosa and submucosa, catgut, gelatin, highly purified calf skin collagen,‡ beef serosa and submucosa, and synthetic films prepared from purified beef tendon.

All of the ultraviolet spectra were measured with a Beckman spectrophotometer (model DU) with ultraviolet attachment. A Coleman spectrophotometer set at 420 mμ was used in the colorimetric determination of tyrosine according to Block and Bolling [5].

Hydrolysis of the collagen was carried out by incubation in a boiling water bath for one hour in either 6 N HCl or 6 N NaOH. Anaerobic hydrolysis

*Aided by a grant from Ethicon Suture Laboratories, Inc.
†With the technical assistance of Mr. Roy M. Sachs and Mrs. Alicia Wayne.
‡Kindly supplied by Dr. John Highberger, United Shoe Machinery Corporation, Beverly, Massachusetts.

utilized Thunberg tubes after evacuation with a water pump. The hydrolysates were clarified by centrifugation to remove the small amount of elastin which was not dissolved by the hydrolysis procedure.

Results

Of the various methods of producing soluble partial hydrolysates of collagen the most useful were heating the preparation for one hour at 100° in either 6 N HCl or 6 N NaOH. Because of the greater stability of certain of the aromatic amino acids in alkaline solutions [6] the alkaline hydrolysis yielded more reliable results than did the acid one. In a typical experiment the absorption maximum at 275 mμ was much less pronounced in the acid hydrolysate than in the alkaline one, and the tyrosine recoverable in one experiment from the acid hydrolysate was only 0.10 per cent as compared with 0.96 per cent from the alkaline one. For crude collagen preparations contaminated with a small amount of carbohydrate, hydrolysis is accompanied by a mild oxidation, indicated by the development of a brownish color, which is characteristic of the oxidation interaction of carbohydrate and certain aromatic amino acids [7]. Such an oxidative results in a slight decrease in absorption of the hydrolysate throughout the ultraviolet region. This complication can be eliminated by hydrolyzing anaerobically in evacuated Thunberg tubes. In view of the above results, the standard procedure for treatment of collagen preparations before spectroscopic analysis was therefore to hydrolyze them anaerobically for 1 hour in 6N NaOH.

Typical results on the ultraviolet absorption spectrum of alkaline hydrolysates of various tissues of sheep small intestine are shown in Fig. 1. The crude whole intestine and the glandular mucosa absorb strongly with a definite maximum, while the collagenous tissues (serosa and submucosa) absorb much less prominently with no apparent maximum in the curve. A variety of collagenous materials including catgut, beef tendon and serosa, kangaroo tail tendon, gelatin and purified calf skin collagen have been examined spectroscopically. The results obtained are in excellent agreement with the conclusions of Loofbourow et al. [4] as well as Salo [8] that the purer the collagen the less prominent the peak in absorption and therefore the higher the ratio of the minimum to the maximum absorption.

Concentration Effects

In the use of the ratio of minimum to maximum absorption as a measure of the purity of any collagenous material [4], the assumption is tacitly made that this ratio does not vary with concentration of the material, i. e. the relationship between different parts of the absorption curve is independent of concentration. This assumption was confirmed in a spectroscopic study of different dilutions of a standard hydrolysate of sheep submucosa at pH

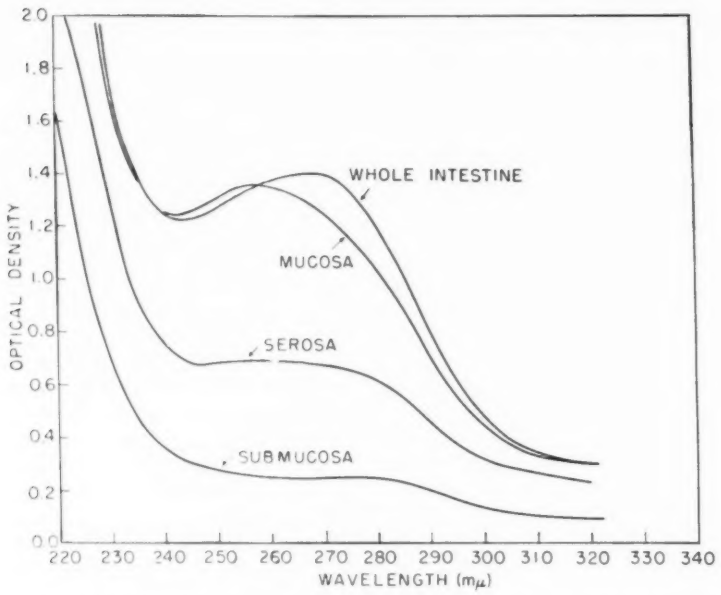

FIGURE 1.—Ultraviolet absorption spectra of hydrolysates of tissues of sheep intestine. The tissues were separated from the crude intestine by mechanical means, hydrolyzed at 100° in 6 N HCl for 30 minutes, then in 6 N NaOH for 30 minutes. The solutions were examined at pH 12 at a final protein concentration of 0.4 mg./ml.

2.65 (Fig. 2). At any selected wavelength the optical density is found from Fig. 2 to increase linearly with protein concentration in accordance with the Beer-Lambert Law. The slope of such straight lines, obtained when density is plotted against concentration, changes with the wavelength used and is greater at the maximum at 275 mμ than at the minimum at 260 mμ. Hence the optical density of the maximum increases with protein concentration much more rapidly than does the optical density of the minimum and the shape of the absorption curve changes sharply with the concentration of collagenous material. It is clear from Fig. 2 that the spectroscopic technique for studying a submucosa hydrolysate at a concentration of 1 mg./ml. is much less sensitive to the presence of a small amount of impurities than it is when used for studying a hydrolysate at a concentration of 5 mg./ml. At low collagen concentrations the resolving power of the Beckman spectrophotometer is not high enough to distinguish between the optical densities at different wavelengths. Since the shape of the curve changes so sharply with

collagen concentration, it is obvious that different preparations should always be compared spectroscopically at the same concentration.

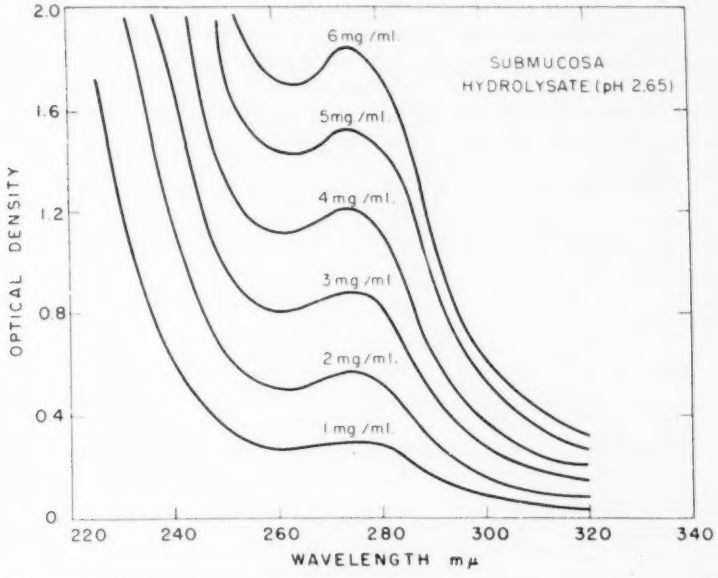

FIGURE 2.—Ultraviolet absorption spectra of sheep submucosa after hydrolysis anaerobically in 5 N NaOH for 2 hours at 112°. The hydrolysate was adjusted to pH 2.65 with HCl and diluted with water to the final concentrations indicated in the figure. This submucosa sample contains 1.23% tyrosine.

The sensitivity of the shape of the ultraviolet absorption curve to concentration is not unique for collagen but applies to other proteins and aromatic amino acids as well as many other compounds. Using tyrosine as an example, it is found that the optical density increases linearly with concentration at both the maximum at 275 mμ and the minimum at 265 mμ, but as is the case with collagen preparations, the rate of increase in absorption with concentration is much greater for the former than for the latter wavelength although the ratio of the absorption at the two wavelengths remains the same.

Total Absorption as a Measure of Purity

On the theory that the ultraviolet absorption of collagen is caused by contamination with proteins containing the aromatic amino acids, it might be predicted that not only would the ratio of minimum to maximum increase with collagen purity, but the total absorption would decrease as well. This

would follow since phenylalanine, tyrosine and tryptophane absorb generally as well as specifically in the region from 240–300 mμ.

The data of Fig. 1 support this thesis, since not only does the prominence of the peak at 275 mμ decrease with collagen purity, but also the total absorption from 240–300 mμ. This hypothesis that general absorption is inversely related to collagen purity is confirmed quantitatively in Fig. 3 where the absorption spectrum of the collagenous material, catgut, is compared with the same material after contamination with 10 per cent bovine serum albumin (Armour). The foreign protein has not only introduced a peak in the absorption curve, but has also appreciably increased the optical density throughout the ultraviolet. An analysis of over 100 different studies of col-

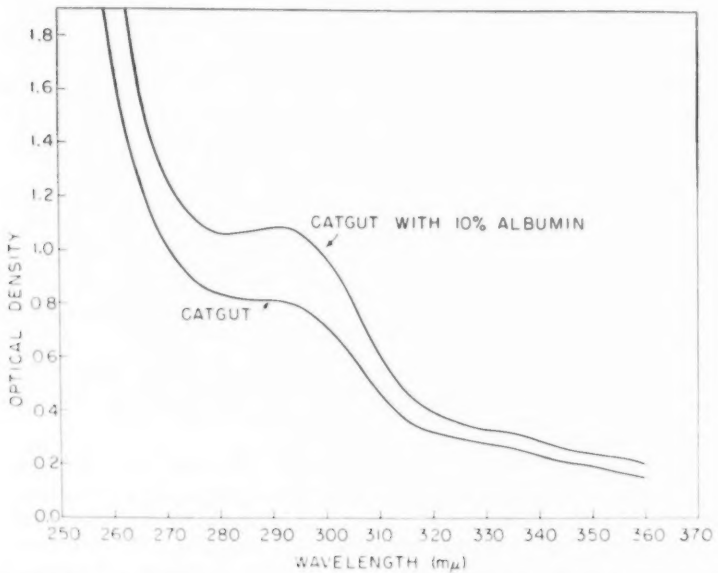

FIGURE 3.—Absorption spectrum of catgut (Ethicon, plain) compared with catgut contaminated before hydrolysis with 10% bovine serum albumin (Armour). Hydrolysis was carried out for 2 hours at 100° in 0.1 N NaOH. The final solutions contained 5.6 mg. protein/ml. at pH 12.

lagenous materials indicates that without exception the purer preparations show a diminished absorption peak and a much lower general absorption throughout the ultraviolet than do cruder preparations. Information on this latter point from the data of Loofbourow et al.[4] is generally not available, since protein concentrations are usually not reported. An analysis of their

data does indicate, however, that purified rat tail collagen (0.076 per cent) absorbs much less throughout the ultraviolet than does crude beef tendon (0.1 per cent) which in turn absorbs more than beef tendon (0.1 per cent) extracted once with Na_2HPO_4. A study of Salo's data [8] on ichthyocol reveals that the collagen purified by electrodeposition absorbs throughout the ultraviolet much less per mg. N than do the impurities which were separated from the ichthyocol. Although the absorption at any arbitrary wavelength from 240–300 mμ might be used as a measure of collagen purity, this method has its maximum sensitivity at 275 mμ, at which wavelength the aromatic amino acids absorb most strongly. This technique (measurement of absorption at 275 mμ) as compared with the minimum/maximum method (ratio of absorption at 260 mμ to that at 275 mμ) is simpler, more sensitive to the detection of absorbing impurities and more applicable to studies of purified collagen preparations for which no peak at 275 mμ is apparent in the absorption spectra.

Tyrosine Determinations

Of the aromatic amino acids in collagen tryptophane is low or lacking [9] and phenylalanine makes a relatively small contribution to absorption, since its absorption is 20 times weaker than tyrosine. Emphasis was therefore placed on estimations of tyrosine in collagen using Bernhardt's modification of the Millon-Weiss method (see 5). Tyrosine determinations on typical collagenous preparations are shown in Table I. There is good general agreement between the ultraviolet and the tyrosine data: collagen preparations adjudged to have a high purity on the basis of low absorption at 275 mμ are found to contain a small amount of tyrosine.

TABLE I

Tyrosine determinations in various collagen preparations as measured chemically and as estimated from the absorptions at 275 mμ, based on the assumption that all the absorption at this wavelength is caused by tyrosine.

Collagen preparation	mg. tyrosine/mg. dry weight preparation	
	Chemical Determination	Estimated from absorption at 275 mμ
Purified calf skin	0.0056	0.019
Sheep submucosa from outer side of intestine	0.012	0.041
Sheep submucosa from inner side of intestine	0.0094	0.024
Sheep serosa	0.015	0.046*
Sheep mucosa	0.016	0.082*
Kangaroo tail tendon	0.008	0.038

*Calculated from absorption curves of hydrolysates (0.4 mg./ml.) at pH 12, while the remaining figures were for hydrolysates (4.0 mg./ml.) at pH 2.

In the absence of other absorbing substances tyrosine can be estimated from the absorption of proteins at 275 mμ. The amount of tyrosine in the collagen hydrolysates has been estimated on the assumption that all of the absorption at 275 mμ is due to tyrosine (Table I). This assumption is clearly incorrect, since the tyrosine estimated from ultraviolet absorption is several times as great as that measured by the chemical method. Since the chemical procedure is believed to be quite reliable, the discrepancy must mean that tyrosine accounts for only a fraction of the absorbing impurities in a typical collagen preparation and that the residual ultraviolet absorption must be due to tryptophane, phenylalanine, and other absorbing impurities such as nucleic acids. Work is in progress to identify and measure the amounts of these non-tyrosine absorbing compounds in collagen preparations.

Collagen Films

Since it is very difficult to prepare clear solutions of mammalian collagen, Loofbourow et al.[4] proposed the use of transparent films prepared by spreading a homogenate of collagen in 1 per cent acetic acid on a plate and evaporating off the solvent. No attempt was made by these investigators, however, to directly compare spectra of collagen solutions with films prepared in this way.

We have found that partially or extensively cleaned ribbons of submucosa or serosa of the small intestine of sheep or cattle are sufficiently transparent for direct examination in the ultraviolet. A longitudinal* strip of ribbon is glued over the window of the Beckman cuvette with a few drops of water, then permitted to dry before the absorption spectrum is measured. A unit area of the dry ribbon is weighed in order to calculate wt./cm.^{2} which is equivalent to wt./ml. for the hydrolysate. Typical results on the absorption at comparable concentrations of a submucosa ribbon and its alkaline hydrolysate (adjusted to pH 2.0) are presented in Fig. 4. The absorption curves are in general similar but not identical, and it is usually found that the ribbon absorbs somewhat more strongly than the hydrolysate. This difference may be explained by the fact that in the preparation of the hydrolysate a small amount of insoluble material is removed before spectroscopic study, while in the ribbon this insoluble component is included and contributes to the absorption.

A study of absorption as a function of concentration may be made by building multifilms made up of several strips of ribbon instead of one. Results obtained in this study are in every way comparable to the concentration studies made with collagen hydrolysates (Fig. 2). Comparisons between the absorption spectra of films and their hydrolysates have also been made using synthetic films of beef tendon collagen prepared according to Loof-

*Since the collagen fibrils are not oriented completely at random the birefringence (which affects the measured absorption) is slightly different along than across the ribbon.

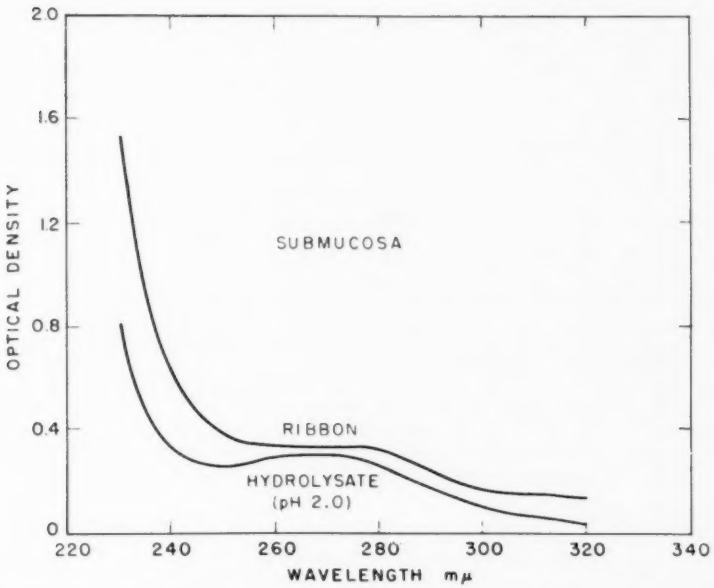

FIGURE 4.—Comparison of the absorption spectrum of a transparent submucosal ribbon (0.62 mg./cm.^{2}) with its hydrolysate (0.62 mg./ml.) after digestion for 1 hour at 100° in 5 N NaOH. The final acidity of the hydrolysate was adjusted to pH 2.0 with HCl.

bourow et al.[4]. Results were in good agreement with those on the natural ribbons. A limitation of the film technique is that the membrane, either natural or synthetic, must be transparent; due to light scattering, translucent, or cloudy films (even when coated with a solvent of high refractive index such as glycerol) were found to absorb more strongly than predicted, and the resultant absorption curve was unspecific and unreliable as an index of collagen purity.

Summary

Anaerobic hydrolysis of collagen in 6 N alkali at 100° is satisfactory for preparing collagen for spectroscopic study in the ultraviolet. The ratio of the minimum in absorption at 260 mμ of collagenous preparations to the maximum at 275 mμ is directly related to collagen purity, but measurements made at high collagen concentrations provide a much better index of purity than data obtained for dilute collagen solutions. The total absorption at 275 mμ is a measure of the amount of impurities in a collagen preparation.

The tyrosine content of a collagen preparation is found to be a good index of the amount of impurities present. Tyrosine accounts for only a fraction of the impurities which are responsible for the absorption of a collagen preparation at 275 mμ. Natural or artificial transparent membranes of collagen are suitable for ultraviolet spectroscopy without preliminary hydrolysis, and are characterized by absorption spectra which are similar to those of hydrolysates.

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Received July 28, 1952.

Treatment of Leather with Polyisobutylene

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Abstract

A laboratory procedure is described for impregnating vegetable-tanned crust leather and chrome-retanned shoe upper leather with polyisobutylene (Vistanex). The treatment consists in immersing dry leather in a solution of Vistanex at room temperature for a specific period, wiping off the excess solution, and evaporating the solvent. The amount of Vistanex deposited in vegetable-tanned crust leather varies from about 13 per cent to 18 per cent of the oven-dry leather. For treating sole leather the most satisfactory molecular-weight range of Vistanex is in the approximate range of 50,000 to 100,000.

Different solvents influence the viscosity of Vistanex solutions, but do not affect the amount of Vistanex deposited in leather. Hence the degree of molecular extension is not a factor in the deposition of Vistanex.

Cationic, and nonionic surface active agents were tried, but none of them affected the amount of Vistanex deposited.

The water absorption of vegetable-tanned crust leather which has been treated with Vistanex is only about half that of untreated specimens. Abrasion resistance is improved from 100 to 160 per cent, depending on the treatment. Limited service tests show that the treated leather wears approximately 80 per cent longer than high quality sole leather.

1. Introduction

Previous papers [1] have shown that certain properties of leather can be improved by impregnating with synthetic resins or natural rubber. The chief advantages gained are a doubling of the abrasion resistance of sole leather and halving of water absorption and water transmission without adversely affecting flexibility or water vapor permeability.

A polymer solution for impregnating leather must have a sufficiently high concentration to deposit the desired amount of solids within the leather; the mean molecular weight of the solute and the solids content of the solution must be adjusted so that the viscosity of the solution will permit penetration into the leather in a reasonable time; and the molecular weight of the solute must be low enough to prevent filtering action at the leather surfaces.

This paper is a report on polyisobutylene (Vistanex) as an impregnant for leather. This polymer is relatively cheap, is soluble in a variety of solvents, and is abundantly available over a wide range of molecular weights. On the basis of previous work [1] it was anticipated that polyisobutylene in the approximate molecular weights range of 50,000 to 100,000 would be suitable for solvent impregnation of vegetable-tanned crust leather as well as lighter leather*

In order to facilitate impregnation, ungreased, unloaded, and non-compacted leather was chosen, such as vegetable-tanned crust leather for sole leather comparisons, and degreased chrome-retanned leather for shoe upper leather comparisons. Impregnation of heavy leather with natural rubber was facilitated by removing a grain split of 30–45 mils [1]. Accordingly, all heavy leather specimens reported in this study were degrained.

Briefly, the treating process consists of immersing air or oven dry leather in a solution of polyisobutylene at room temperature for a specified time, wiping off the excess solution, and evaporating the solvent. Further details of the solvent method for impregnating leather with polyisobutylene follow in section 4.

Other methods of impregnating leather with polymers have been reported. Since polyisobutylene is soluble in oils, Frolich [2] and Chadwick [3] suggested that it be introduced into leather with the grease normally used.

Cheronis [4] employed polymer emulsions for impregnating chrome-tanned horsehides for gloves. He reported that properly stabilized emulsion polymer suspensions deposit 20–40 per cent of various resins, silicones, and synthetic elastomers.

2. Preparation of Vistanex Solutions

Vistanex solutions suitable for impregnating leather may be prepared by simple mixing of the appropriate solvent and Vistanex of the proper molecular

*Polyisobutylene in this molecular weight range is sold as Vistanex LM-H and LM-MS by the Enjay Company, 125 Broad Street, Elizabeth 4, New Jersey. To the best of the author's knowledge this is the only source of polyisobutylene in this range of molecular weights.

weight range. It was found convenient to weigh Vistanex and solvent into friction top cans, which also served as suitable containers in which to treat leather specimens. The solution was effected by placing the tightly closed cans in a rotary mixer. The solution time varied from a few hours to several days, depending on the concentration and molecular weight of the Vistanex. For sole leather, Vistanex grades LM-MS or LM-H are most suitable and may be used with several different solvents. The commercial availability of Vistanex in molecular weight grades suitable for impregnating leather is a distinct advantage over natural rubber, which requires extended cold milling to obtain proper molecular breakdown and low viscosity solutions of high solids content [1].

Table 1 shows the viscosities of solutions made with Vistanex of several grades, using different solvents and different concentrations. The concentrations or solids content of all Vistanex solutions are on a weight basis,

TABLE I

Viscosities of Vistanex Solutions*

Solvents	density g/ml	Vistanex Grades: B-60 15% solids poises	B-40 20% solids poises	B-40 + LM-H (1:1) 30% solids poises	LM-H 30% solids poises	LM-H 40% solids poises	LM-MS 30% solids poises	LM-MS 40% solids poises	LM-MS 50% solids poises	LM-MS 60% solids poises
Gasoline	0.66	56.9	26.2	45.0	2.5	13.8	——	4.4	17.5	——
Stoddard solvent	0.79	96.9	41.3	79.4	4.4	21.3	1.3	6.2	30.6	——
Toluene	0.87	28.8	16.9	31.3	1.9	9.4	——	3.1	11.3	——
Chloroform	1.50	25.0	10.6	19.4	1.3	5.6	——	1.9	6.9	——
Trichloroethylene	1.46	——	11.3	18.1	——	5.6	0.6	1.9	6.2	87.5
Carbontetrachloride	1.60	——	23.1	41.8	——	12.5	——	——	——	——
Stoddard solvent Chloroform (4:1)	——	142.5	35.0	——	——	16.2	——	4.4	——	——

*Measured with a Gardner bubble viscometer at 73° F.

using gasoline as a reference solvent. The weights of all other solvents used for making solutions of Vistanex were adjusted so that the volume fraction of the solvent was the same for all solutions of corresponding concentrations. The density values given in Table 1 were used for calculating the adjustments.

The molecular weights of different lots of Vistanex of the same grade may vary widely as shown by a variation of 50 per cent in the intrinsic viscosity. The viscosity average molecular weights of the Vistanex grades investigated follow:

Vistanex B60 — 400,000
Vistanex B40 — 266,000
Vistanex LM-H — 110,000
Vistanex LM-MS— 69,000

3. Factors Influencing Viscosity of Vistanex Solutions

It is well known that the viscosity of polymer solutions increases with increasing molecular weight and concentration, that the viscosity may increase or decrease with increasing temperature, and that the viscosity varies widely with different solvents. An understanding of these viscosity relations will aid in studying the impregnation of leather with polymer solutions. Accordingly, the main factors which influence viscosity are briefly reviewed.

Flory[5] has shown experimentally that the intrinsic viscosity of polyisobutylene, ranging in molecular weight from 10^4 to 10^6, is proportional to its molecular weight raised to the 0.64 power. Huggins[6] has demonstrated theoretically that the power in the above relation is intimately related to the general shape of the dissolved polymer molecule. If the molecule is tightly coiled into a sphere, the power would be zero; if the polymer molecule is rigidly extended as a rod, the power would be 2; and if the polymer molecule is extended at random, the power would be 1. The value of 0.64 for polyisobutylene has been interpreted to signify that it has a mean shape intermediate between that of random extension and spherical molecules. Huggins has also interpreted the wide variation of intrinsic viscosity obtained with different solvents as a result of varying degrees of curling of the dissolved polymer molecule. Hence, in a poor solvent curling is favored and intrinsic viscosity is low, while in a good solvent a greater mean molecular extension is favored and the intrinsic viscosity is high.

According to Arrhenius' equation, the logarithm of the relative viscosity of a polymer solution is proportional to polymer concentration. This relation is only approximately valid and has been modified by numerous workers, but, in general, the viscosity of a polymer solution can be quite well expressed as a power series of the concentration using only two constants. Evans and Young[7] studied the viscosity of polyisobutylene (molecular weight 104,000) in 60 different solvents of several classes. In general, they found Arrhenius' relation valid up to concentrations of about 7 per cent.

Alfrey[8] has shown that an increase in temperature generally lowers the specific viscosity of polystryrene solutions in good solvents, but increases the specific viscosity in poor solvents. He interprets these temperature-viscosity relations in terms of additional curling or uncurling of the dissolved polymer molecules. Alfrey also reported that when polymers are dissolved in poor solvents at low concentrations, within chain contacts are favored by the tightly coiled molecules, but at higher concentrations chain-to-chain contacts

are favored with resulting gel formation. On the other hand, the good solvents with a high intrinsic viscosity will tolerate a higher polymer concentration before gelling than the poor solvents. A good solvent forms a solvated hull around the individual chains at low concentration, which hinders within-chain contacts and probably also hinders chain-to-chain contacts so that gel formation does not occur as readily as with poor solvents.

Huggins[9] has shown that aggregation of dissolved polymer molecules occurs at a concentration somewhat lower than for phase separation. Hence, the slope of the viscosity versus concentration curve decreases or becomes negative as the concentration approaches the precipitation point. As would be expected for a good solvent, this anomalous effect disappears at a higher temperature.

The viscosity relations discussed above apply primarily to dilute polymer solutions. Fundamental knowledge of concentrated solutions is much more limited. Ferry and Ashworth[10] studied the rigidities of concentrated solutions (up to 29 per cent) of polyisobutylene, and concluded that in concentrated as well as in dilute solutions the average volume pervaded by a dissolved polymer molecule is less for a solution of low intrinsic viscosity than for a solution of high intrinsic viscosity. They extended Kuhn's theories[11] on deformation and rigidity of polymers in dilute solutions to concentrated solutions, and presumed a similar transitory network structure whose net points are entanglements where two chains happen to be tightly kinked about each other. They postulated that in concentrated solutions the domain pervaded by a polymer molecule is thoroughly interlaced by other molecules, and that the entanglement probability should be practically independent of the size of the coil domain, but markedly influenced by local chain configuration, back-kinking, snagging, etc.

For impregnating leather with polyisobutylene, concentrated solutions are necessary to obtain large depositions within the leather. Fortunately, polyisobutylene is highly soluble, particularly in hydrocarbons. Flory[5] interpreted this high solubility as being due to the linear character of polyisobutylene and the virtual absence of crosslinks or branching.

An examination of Table I shows that chloroform and trichloroethylene form Vistanex solutions of approximately equally low viscosity. For the hydrocarbon solvents, the order of increasing viscosity is toluene, gasoline, and Stoddard solvent. Low viscosity is generally associated with highly curled polymer molecules and poor solvents, as discussed above. The addition of poor solvents to polymer dissolved in good solvents generally lowers the viscosity. Thus it was found that an inverse linear relation exists between the logarithm of the viscosity of 50 per cent Vistanex LM-H solutions and the amount of chloroform used (up to 75 per cent) in Stoddard solvent-chloroform mixed solvents. Table 1 shows that the addition of chloroform

to Stoddard solvent solutions of Vistanex lowers the viscosity in all cases except that of Vistanex B-60. Vistanex B-60 has the highest molecular weight investigated (estimated to be 400,000), and therefore it is suggested that the addition of a poorer solvent such as chloroform could cause the observed rise in viscosity, because at 15 per cent solids the solution may be nearing the point of incipient gel formation. Or, in terms of Alfrey's work, it might be said that for the large B-60 molecules the addition of chloroform favors curling of the polymer molecules so that a considerably larger number of chain-to-chain contacts are made than with lower molecular weight polyisobutylene, and therefore the concentration for incipent gel formation may be effectively lowered by the addition of chloroform and thus account for an increase in viscosity by the chloroform instead of the expected decrease in viscosity.

4. Deposition Results

Preliminary results showed that 40 per cent solutions of Vistanex LM-H and LM-MS in gasoline deposited about 15 grams of polyisobutylene per 100 grams of degrained vegetable-tanned crust leather. Further experiments were directed toward deposition of as much polyisobutylene of as high molecular weight as possible under conditions which would be commercially feasible.

4.1 Effects of Different Molecular Weights of Vistanex, Different Solvents, and Different Surface Active Agents.

The effect of four different solvents, four surface active agents, and four molecular weights of Vistanex on the amount of Vistanex deposited in vegetable-tanned crust leather were efficiently evaluated by a 4 x 4 latin square experiment. The 16 sets of duplicate specimens necessary for the experiment were selected by means of random numbers so that specimen-to-specimen variation was distributed as equally as possible among the various treatments.

The solvent types selected were aliphatic and aromatic hydrocarbons, a chlorinated hydrocarbon, and a mixture of a chlorinated and an aliphatic hydrocarbon. The anionic type of surface active agent was represented by Aerosol OT (dioctyl ester of sodium sulfosuccinic acid); the cationic type was represented by Alkaterge C (a substitute oxazoline); and the nonionic type was represented by Emulphor ON (an ethylene oxide condensate).

The data from the latin square experiment are presented in Tables 2 and 3. These data were subjected to an analysis of variance, which show . . . that there is a significant difference in extent of deposition by B-60 and B-40 Vistanex on the one hand and LM-H and LM-MS on the other; it shows that there is no significant effect on deposition of Vistanex due to the surface active agents used; and it also shows no significant effect on deposition of

Vistanex due to the different solvents. From these data it appears that there is a critical molecular size somewhere between Vistanex B-40 and LM-H. Other data in section 4.2 are not in agreement with a critical molecular size in this range. The difference in deposition obtained with the low and high molecular weight pairs of Vistanex can not be accounted for on the basis of solids content. Another experiment will be described with solutions of Vistanex B-40 and LM-H in which the solids contents are equal.

TABLE 2

Deposition of Vistanex in Degrained Vegetable-Tanned Crust Leather

Solvent	Deposition by Vistanex Solutions of Different Grades and Concentrations			
	B-60 15 Per cent*	B-40 20 Per cent*	LM-H 40 Per cent*	LM-MS 40 Per cent
Chloroform	−1.8	0.8	18.9	13.7
Toluene	0.5	−1.0	20.3	23.3
Stoddard solvent	2.1	2.4	21.7	15.0
Stoddard solvent & chloroform (4:1)	1.8	3.5	17.9	19.4

*Each value is the mean of two specimens.

TABLE 3

Deposition of Vistanex in Degrained Vegetable-Tanned Crust Leather

Solvent	Deposition by Vistanex Solutions Containing Surface Active Agents			
	Alkaterge C Per cent*	Emulphor ON Per cent*	Aerosol OT Per cent*	None Per cent*
Chloroform	−1.8	0.8	18.9	13.7
Toluene	−1.0	0.5	23.3	20.3
Stoddard solvent	21.7	15.0	2.1	2.4
Stoddard solvent and chloroform (V:1)	19.4	17.9	3.5	1.8

*Each value is the mean of two specimens.

The lack of solvent effect shows that neither viscosity nor molecular shape were significant factors in deposition because the viscosity of corresponding Vistanex solutions varied widely, as shown in Table I. The magnitude of the viscosity of polymer solutions is indicative of the shape or mean molecular extension of dissolved polymer molecules.

4.2 Effect of Stepwise Increase in Molecular Weight of Vistanex on Deposition

Table 4 shows the results of an experiment with degrained vegetable-tanned crust leather and 30 per cent solutions of Vistanex in gasoline in which the composition of the solute varied in seven steps from 100 per cent, B-40, to 100 per cent, LM-H. It is apparent from the last column of Table 4 that for 20 hours immersion the extent of deposition was affected by neither the composition of solute nor the solution viscosity. For the 30 per cent solutions used it appears that, if the immersion period is sufficiently long, Vistanex B-40 or polyisobutylene with an estimated molecular weight of 266,000 can be deposited in degrained vegetable-tanned crust leather to the same extent as Vistanex with a molecular weight of 110,000, but the extremely high viscosity of the B-40 solution makes it impractical to use.

TABLE 4

Viscosity and Deposition Results of Solutions of 30 Per cent Vistanex in Gasoline with Solutes of Various Compositions

Composition of Solute		Viscosity	Deposition for Immersion Period	
Vistanex, Per cent		poises	2 hr Per cent	20 hr Per cent
100 B-40,	0 LM-H	526	1.1	6.0
80 B-40,	20 LM-H	216	1.9	6.6
65 B-40,	35 LM-H	103	2.6	7.3
50 B-40,	50 LM-H	50.0	3.8	6.4
35 B-40,	65 LM-H	18.7	5.9	6.2
20 B-40,	80 LM-H	10.0	6.6	6.5
0 B-40,	100 LM-H	2.5	6.8	6.5

Since the extent of deposition was the same for both polymers, and since gasoline solutions have higher viscosities than corresponding chloroform solutions, the deposition results suggest that the more extended shape of even the high molecular-weight Vistanex B-40 does not interfere with penetration into leather.

The third column of Table 4 shows that for a 2-hour immersion period the deposition of Vistanex in leather is an inverse function of the solution viscosity down to viscosities below 30 seconds.

Figure 1 is a log-log plot of solution viscosity against deposition of Vistanex for 2 *hours immersion*. The negative slope of the linear portion of the curve signifies a hyperbolic relation between viscosity and deposition. The linear

part of the curve may be expressed by the flow equation, log deposition = K log η + C, where η is the solution viscosity, and C is the deposition intercept. The constant K, as a measure of slope, is closely associated with pore size of the leather. For fixed viscosities, surface tension, temperature, etc., an increase in pore size of the leather would be expected to increase K, because as the pore size increases the volume rate of flow of solution into the leather would also be expected to increase, which would in turn increase the deposition of Vistanex in the leather and thereby cause K to increase. Extrapolation of the lower end of the curve shows that theoretically 1 per cent deposition would occur in 2 hours from a solution whose viscosity was approximately 700 poises. A hypothetical value of 27 may be obtained for C in the above equation by extrapolating the linear portion to $\eta = 1$. However, such an extrapolation has no physical meaning because as the solution viscosity becomes lower the leather becomes saturated in less than 2 hours and therefore large deviations from linearity result. A similar linear plot would probably be obtained for solutions of lower viscosity if the immersion period was shorter.

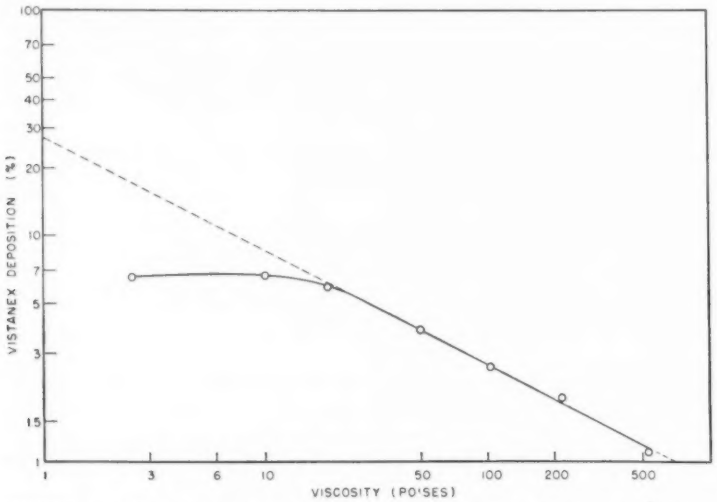

FIGURE 1.—Effect of viscosity of impregnating solution on the amount of Vistanex deposited in 2 hours' immersion. Each point is the mean of two specimens.

4.3 Effects of Time and Concentration on the Deposition of Vistanex

Table 5 and Figure 2 show the amounts of Vistanex LM-MS and LM-H deposited in degrained vegetable-tanned crust leather from trichloroethylene

solutions during several immersion periods. The 10 per cent and 20 per cent curves exhibit maximum depositions at half-hour immersion periods followed by an "apparent downward trend". A suggested explanation for this apparent downward trend is that diffusion of the grease can readily occur in these dilute and very fluid solutions. In other words, equilibrium between the leather and solution is quickly established, and since the solution is predominately solvent, leaching and diffusion of the grease and tannins can easily occur.

TABLE 5

Deposition Results from Solutions of Vistanex LM-MS and LM-H in Trichloroethylene

Impregnating Solution			Deposition of Vistanex for Different Immersion Periods							
Type of Vistanex	Solids content	Viscosity	½ hr	1 hr	2 hr	4 hr	7 hr	18 hr	48 hr	144 hr
	%	poises	%*	%*	%*	%*	%*	%*	%*	%*
LM-MS	10	0.62	2.2	1.2	−0.3	−0.2	−0.7	——	——	——
LM-MS	20	0.62	6.5	6.2	4.2	6.0	3.1	3.5	——	——
LM-MS	40	3.1	14.0	14.3	14.6	14.1	13.3	13.8	——	——
LM-MS	60	87.5	11.2	13.6	15.3	20.8	28.4	26.7	35.0	28.8
LM-MS	70	816	——	——	13.2	13.8	17.0	21.4	35.9	32.3
LM-H	60	409	6.3	——	——	——	——	24.0	30.3	27.1

*Each value is the mean deposition of two specimens.

Figure 2 indicates that the 40 per cent solution is either too viscous or too concentrated for a downward deposition trend to appear in 18 hours. The upward trend continues for the 60 and 70 per cent solutions up to 48 hours and then appears to fall off at 144 hours. Table 5 shows a corresponding drop in "apparent deposition" for the LM-H grade of Vistanex between 48 and 144 hours immersion period. Although there is insufficient data in Table 5 for statistical proof of maximum depositions for the 60 and 70 per cent solutions, and although there are no deposition periods beyond 144 hours to establish trends, nevertheless the fact that a decline occurred in each of three independent experiments is strong evidence that the maxima are real and not due to experimental error. In these cases it is suggested that the delay in reaching equilibrium between the solution and the leather, as well as the subsequent falling off of deposition, is due to the high viscosity and concentration of the impregnating solutions. Thus it appears that if sufficient time is allowed the same type of deposition curves are obtained for Vistanex solutions of high concentration and viscosity as for solutions of low concentration and viscosity.

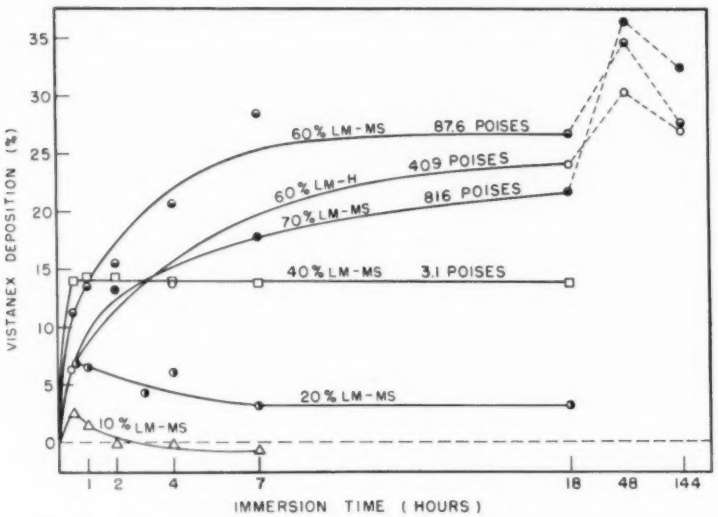

FIGURE 2.—Effect of time on the amount of Vistanex deposited by solutions of Vistanex in trichloroethylene whose concentration ranged from 10 to 70 per cent solids. Each point is the mean of two specimens.

4.4 Deposition of Vistanex in Shoe Upper Leather

Degreased chrome-retanned upper leather can easily be treated with polyisobutylene. Thirty per cent of Vistanex LM-H dissolved in gasoline is a suitable impregnating solution. Sixteen-hour immersion in such a solution results in a mean deposition of 26 per cent Vistanex.

4.5 Treatment of Vegetable-Tanned Crust Leather with Vistanex LM-H for Service Tests

In order to make a preliminary service test, eighteen soles were cut from vegetable tanned crust leather bends, matched to the corresponding finished sole leather bends from the same butt bends. Grain and flesh splits were removed from the crust soles, of approximately two and one ounces, respectively. The soles were treated with 40 per cent solutions of Vistanex LM-H in gasoline for 16 hours at room temperature. The mean Vistanex constant of the 18 treated soles was 18.4 per cent of the weight of the oven-dry soles.

A large scale laboratory treating process was established for treating 72 pairs of degrained and defleshed vegetable-tanned crust leather soles with solutions of 40 per cent Vistanex LM-H in gasoline. Two treating baths, approximately 14 inches long by 6 inches wide by 8 inches high, were used

to accommodate six pairs of soles each. In order to assure that the Vistanex solutions had access to all areas of the soles, 4-mesh wire grid separators were used between the soles in the treating baths. The impregnation was carried out at room temperature for a period of approximately 16 hours.

Six pairs of soles for treatment were cut from each bend as shown in Figure 3. The bends were not matched, but were selected to range from about 8½ to 9½ pounds and were nearly free of brands and cuts.

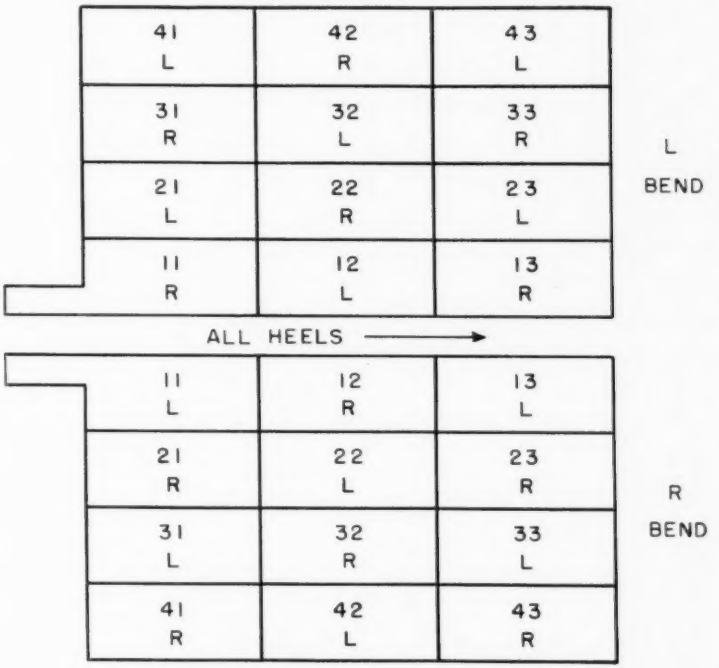

FIGURE 3.—Pattern used in cutting soles from bends.

The bend averages ranged from 15.7 per cent to 20.4 per cent of deposited Vistanex. The position averages as well as the bend-to-bend standard deviations for each position are shown in Table 6. As would be expected, the data show that, in general, the deposition of Vistanex increases from backbone to belly and from tail to shoulder. An analysis of variance shows that the bend-to-bend variance is slightly greater than the position-to-position variance, and that both bends and position effects on the amount of Vistanex deposited are significant. Figure 4 is a graph of the data in Table 6 and

suggests that a trend or linear relation exists between the mean position deposition and bend-to-bend standard deviation for corresponding positions.

TABLE 6

Deposition of Vistanex by Location within Bends
(Data based on 12 bends)

Location	11	12	13
Mean deposition (%)	15.1	16.9	17.4
Std. Dev. (%)	1.0	1.2	0.9
Location	21	22	23
Mean deposition (%)	16.5	17.9	18.4
Std. Dev. (%)	1.4	1.4	1.6
Location	31	32	33
Mean deposition (%)	18.0	19.1	19.2
Std. Dev. (%)	1.6	1.4	1.3
Location	41	42	43
Mean deposition (%)	18.8	19.1	19.6
Std. Dev. (%)	2.0	1.8	1.6

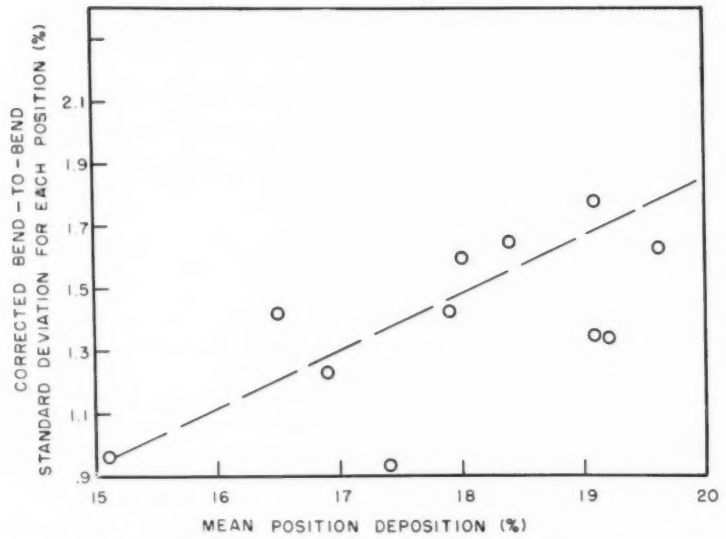

FIGURE 4.—Relation between the bend-to-bend standard deviation and the mean position deposition. Each point represents 12 soles.

5. Properties of Treated Leather

Unless otherwise specified, all tests were carried out in accordance with Federal Specification KK-L-311 for Leather and Leather Products; General Specifications (Methods of Sampling, Inspection and Tests).

5.1 Water Absorption

Figure 5 shows water absorption curves for untreated vegetable-tanned crust leather and for the same type of leather subjected to several different Vistanex treatments. Inspection of the upper three curves shows that 7–8 per cent Vistanex consistently reduces water absorption for all periods, and that Vistanex LM-H is superior to LM-MS. The lower two curves indicate that although during the early periods of the test 31 per cent of Vistanex LM-MS reduces water absorption by a larger amount than 17 per cent of Vistanex LM-H reduces it, the two curves approach the same equilibrium value. The amount of absorption at 24 hours for both of these treatments is about half that of the untreated leather. By a series of t-tests it was demonstrated that all treatments significantly reduce water absorption for 24 hours. Moreover, these improvements are manifest at the half-hour absorption period as well, and in addition, all the half-hour points in Figure 5 are significantly different from each other. However, for the 24-hour period there are no significant differences between the upper two treatments or between the lower two treatments.

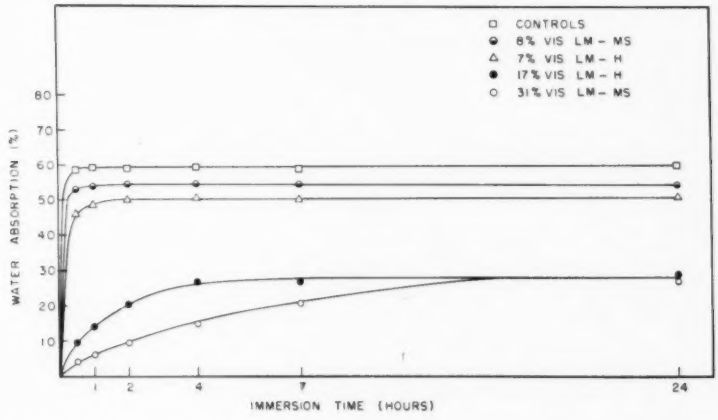

FIGURE 5.—Effect of different Vistanex treatments on the water absorption of vegetable-tanned crust leather. Each point is the mean of three specimens.

5.2 Abrasion Resistance

Abrasion tests were performed as prescribed in the aforementioned specification, except that the load on the prony brake was reduced from 20 to 10 pounds and the load required to lift the wheel at point A of Figure 15 was reduced from 36 to 26 pounds.

The curves in Figure 6 show the comparative abrasion resistance of untreated vegetable-tanned crust leather and the same type of leather subjected to three different Vistanex treatments. These treatments were chosen with the view of determining the differences in improvement of abrasion resistance caused by treating leather with different amounts of Vistanex LM-H, and a blend of Vistanex B-40 and LM-H. For a gasoline solution containing 30 per cent of Vistanex solids, only about 1 part of Vistanex B-40 to two parts of LM-H could be used and still maintain the viscosity of the impregnating solution at a feasible level. Figure 6 indicates the level at which 60 per cent of the original thickness of the leather has been abraded, as well as an adjusted 60 per cent abrasion loss. The 60 per cent loss was adjusted to account for the fact that approximately 45 mils were split from the grain surfaces of the treated specimens. This 10 mils adjustment was calculated from the slope of the straight portion of the abrasion curve and the revolutions required to abrade the 45-mil grain from the controls.

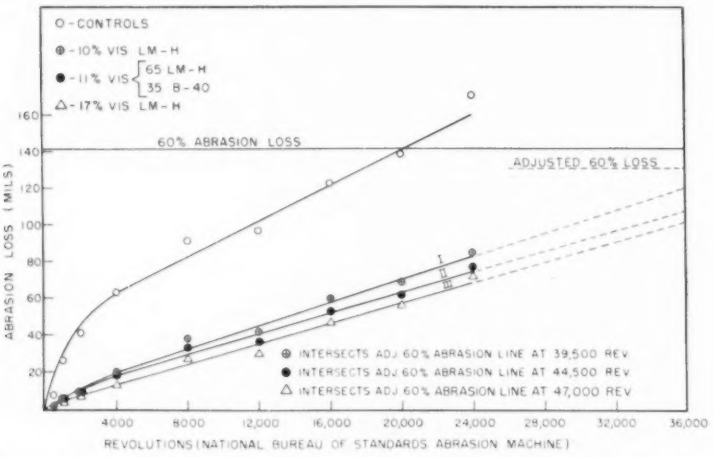

FIGURE 6.—Effect of different Vistanex treatments on the abrasion resistance of vegetable-tanned crust leather. Each point is the mean of three specimens.

Extrapolation of the abrasion curves for the treated specimens to the adjusted 60 per cent abrasion line indicates the number of revolutions which

would be required to abrade them to the same extent as the controls. All treatments showed an improvement of about 100 per cent or more. The abrasion losses for each 4000 revolutions were tabulated for each treatment. By making t-tests on these sets of differences it was shown that . . the abrasion rates for treatments I and II are significantly different, but the rates for II and III are not significantly different. Despite these statistical differences the relative improvements for all treatments are essentially the same. From a development viewpoint, such factors as costs and viscosity of the treating solutions, which make for easy or difficult processing, would probably be the deciding factors.

Another experiment was designed to determine the differences in improvement of abrasion resistance due to different amounts of Vistanex LM-MS, and also to compare approximately equal amounts of Vistanex LM-MS and LM-H.

The curves in Figure 7 show the abrasion results obtained. Inspection of the graph indicates that 14–15 per cent of either Vistanex LM-MS or LM-H slightly more than doubles the abrasion resistance of vegetable-tanned crust leather. A deposition of 23 per cent Vistanex LM-MS causes relative improvement of 160 per cent in abrasion resistance over that of untreated leather. The superior abrasion resistance obtained by treatment with 23 per cent of Vistanex LM-MS over the other Vistanex treatments is clearly demonstrated by a t-test of the values obtained from the intersections of the adjusted 60 per cent abrasion line and the lines representing the abrasion losses for each specimen.

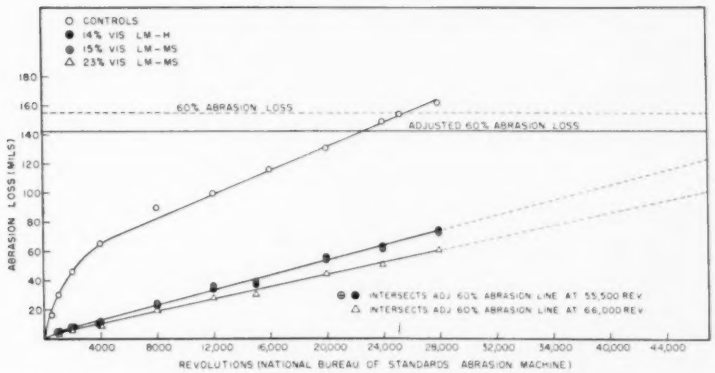

FIGURE 7.—Effect of different Vistanex treatments on the abrasion resistance of vegetable-tanned crust leather. Each point is the mean of three specimens.

5.3 Service Tests

Service tests were designed according to the method of Whitmore and Downing [12]. Each pair of matched bends, consisting of sole and crust leather, was obtained from the same butt bend through the kind cooperation of the Leas & McVitty Company. By cutting one sole of each test pair from a sole leather bend, and cutting the crust sole for treatment from the corresponding location of the matched crust bend, the animal-to-animal and position-to-position variations were virtually eliminated from the comparative wear results of each test pair. The personnel who participated in the service test covered a wide range of occupations. Some of the participants furnished two pairs of shoes so that cross-mated soles could be worn on alternate days. For the participants who furnished only one pair of shoes the cross-mating was necessarily consecutive rather than concurrent.

The end-point of a test pair of soles was considered to have occurred when one sole wore through. The thickness of all soles was measured at the point shown in Figure 8, as well as at the thinnest spots of the sole not worn through. Since the flesh and grain layers were split off prior to treatment, it was considered appropriate to regard the full thickness of the treated sole as uniform with respect to expected wear. This procedure largely overcomes Mitton's [13] objection to the Whitmore-Downing method of making comparative wear tests.

In each of the twelve test pairs of soles returned the Vistanex-treated sole was intact while a hole had worn through the control sole. The degree of improvement due to the Vistanex treatment was calculated from the thickness of the worn treated sole at the thinnest spot according to the equation:

$$\text{per centage of improvement due to treatment} = \frac{\text{mils remaining}}{\text{mils worn}} \times 100$$

The original thickness of the control sole is irrelevant to the calculated improvement. The wear of the treated sole, at the thinnest spot, corresponds to the full wear of the control sole, which may be regarded as the standard of comparison. Hence the remaining thickness of the treated sole, at the thinnest spot, may be regarded as extra potential wear or improvement due to the treatment. The mean improvement was 84 per cent and the 90 per cent confidence limits were 84 ± 18 per cent.

These service test data suggest that a grain split might be taken for upholstery leather, luggage, or other uses where top grain leather brings a premium price, and still permit the production of superior wearing sole leather by impregnating with Vistancy.

The numbers on Figure 8 show the mean wear pattern of the control soles expressed in mils of leather worn away. The bars in Figure 9 graphically represent the same data as Figure 8. The height of the bars, however, are ten times the wear expressed in mils. The figures clearly show that the ball of the foot is the area worn most severely. The wear pattern would also be

of value to indicate the proper placing of reinforcing materials in synthetic shoe soles.

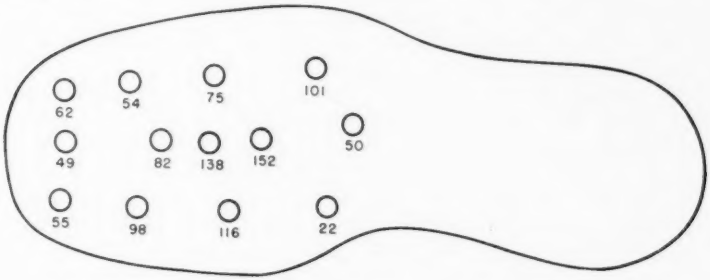

FIGURE 8.—Relative mean wear (mils) of control soles at different positions.

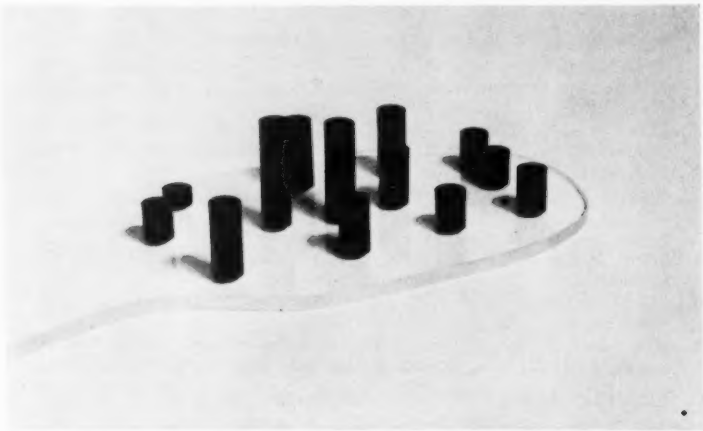

FIGURE 9.—Relative mean wear (mils x 10) of control soles at different positions.

In addition to the above mentioned service test, in which Vistanex treated vegetable-tanned crust leather was compared with high quality sole leather, a similar service test was carried out in which vegetable tanned crust leather was treated with natural rubber [1]. A t-test showed no significant difference between the improvement in durability due to the Vistanex treatment and that due to the natural rubber treatment.

6. Summary

1. A laboratory procedure is described for impregnating vegetable-tanned crust leather and chrome-retanned shoe upper leather with polyisobutylene

(Vistanex) in the molecular weight range of 50,000 to 100,000.

2. Within the molecular weight range of Vistanex recommended different solvents had no effect on the extent of deposition in leather, but the different solvents markedly influenced solution viscosities. Hence molecular shape had no influence on extent of deposition.

3. Single examples of a cationic, an anionic, and a nonionic surface active agent showed no effect on the extent of deposition.

4. Water absorption of vegetable-tanned crust leather treated with 17 per cent Vistanex LM-H is only about half that of untreated specimens.

5. Abrasion resistance of Vistanex treated vegetable-tanned crust leather is improved from 100–160 per cent, depending on the treatment.

6. Limited service tests show that vegetable-tanned crust leather treated with 18 per cent Vistanex LM-H wears approximately 80 per cent longer than high quality sole leather.

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Received June 15, 1952

Note on the Isoelectric Point of Chrome Tanned Collagen

S. G. Shuttleworth and G. E. Cunningham

The change in isoelectric point of collagen resulting from tannage with various chromium complex salts has in the past [1, 2] been used to indicate whether the protein carboxyl or amino groups are involved in chrome tannage. While it is gratifying to note that Gustavson [3] has recently drawn attention to the serious errors in interpretation that can arise through neglecting the effect of complex forming buffer salts, and of drying the stock prior to the

determination of the I.E.P., it does not appear to be generally realized that the direction of the shift in the I.E.P. of collagen as a result of chrome tanning provides no information as to the type of protein groups involved. In fact, it can be shown quite simply that even if only the protein carboxyl groups were involved, and there is considerable evidence in support of this contention [4, 5], the I.E.P. may be raised *or* lowered according to the nature of the initial mean charge on the chrome complexes. It is obvious, therefore, that the direction of the shift cannot be taken to indicate whether acidic or basic protein groups are involved.

While it would seem to be self evident that any alteration in electrical charge on the protein induced by combination with chromium complex ions is sufficient to account for the results of Gustavson [3] and Otto [6], the following considerations may be of interest in that they indicate how a general expression may be deduced for enabling the direction of the shift in I.E.P. to be calculated for any given set of circumstances.

Consider the general case where both the protein acid and basic groups are combined with chromium complex ions. These groups may be identified with the electron donating groups such as $-COO^-$ and $-NH_2$, since the conjugate forms $-COOH$ and $-NH_3^+$ cannot co-ordinate directly with a metal atom. If the initial charge of each type of chromium complex ion combining with the acid or basic groups of the protein is ν_1, ν_2, ν_3 etc., and the number of carboxyl groups combining with each ion type is n_1, n_2, n_3 etc., the corresponding symbols for the number of amino groups being m_1, m_2, m_3 etc., then the following components will be present in unit weight of protein in contact with pure water.

N.	$[P.COO\bar{n}\ .\ Cr]$	$\frac{\Sigma\ p_i(\nu_i - n_i)}{N}$	$[P.\ (NH_2)\ \bar{m}.\ Cr]$	$\frac{\Sigma q_i \nu_i}{M}$	M
a_1	$P.OO^-$		$H_2N.P$		b_1
a_2	$P.COOH$		$H_2N.P.$		b_2
	y^-		x^+		
	OH^-		H		

$a_1 + a_2 + N\bar{n} = A$ (total carboxyl groups)

$b_1 + b_2 + M\bar{m} = B$ (total amino groups)

For electrical neutrality of the whole system the total charge Z on the protein (including hydrions and hydroxyl ions which cannot be dissociated from it, even at the isoelectric point) is given by

$$Z = H^+ + b_1 - a_1 - OH^- + M\bar{\nu}' + N(\bar{\nu} - \bar{n}) = x^+ - y^-$$

where $\bar{\nu}$ and $\bar{\nu}'$ are the average initial charges of the complexes combining with acid and basic groups respectively. Since at the isoelectric point Z is zero and $x = y$, we may write

$$\frac{h - oh}{\alpha_H} = a_1 - b_1 - M\bar{\nu}' - N\ (\bar{\nu} - \bar{n})$$

where h and oh are the hydrogen ion activities at the I.E.P. and α_H is the activity coefficient of the hydrogen ions.

In terms of the "titration" constants K_1' and K_2' of the protein carboxyl groups and the conjugate acid $P.NH_3$ respectively, we have

$$\frac{h - oh}{\alpha_H} = \frac{K_1'(A - N\bar{n})}{K_1' + h} - \frac{h(B - M\bar{m})}{K_2' + h} - M\bar{\nu}' - N(\bar{\nu} - \bar{n})$$

to a first approximation $K_1' \gg h \gg K_2'$, whence the expression simplifies to

$$\frac{h - oh}{\alpha_H} = A - B + M\bar{m} - N\bar{\nu} - M\bar{\nu}'$$

Since in the case of the pure protein alone, the corresponding expression at the isoelectric point is

$$\frac{h - oh}{\alpha_H} = A - B$$

it follows that the difference between these two expressions, is a measure of the shift of isoelectric point in passing from one system to the other. Ignoring differences in the activity coefficient α_H for the two systems we may write

$$D = M\bar{m} - N\bar{\nu} - M\bar{\nu}'$$

and a positive value of D will indicate a decrease in I.E.P. (on the pH scale) while a negative value will indicate an increase.

An exact treatment will of course require consideration of the influence of the change in electrostatic field on the values of K_1' and K_2', which cannot be estimated without an exact knowledge of the molecular configuration[7], but in a qualitative sense such refinements will not seriously affect the main conclusions. It will be noted that for $M = O$ (no amino groups involved) cationic complexes with a positive value of $\bar{\nu}$ will result in an increase in isoelectric point, anionic complexes causing a decrease.

The rule may be illustrated by reference to actual examples as follows:

Example 1

$$M = O;\ \bar{\nu} = +2;$$
$$P.COO^- + (Cr.\ etc.)^{++} \rightarrow P.(Cr\ etc.)^+$$
I.E.P. raised

Example 2

$$M = O;\ \bar{\nu} = +1;$$
$$P.COO^- + (Cr\ etc.)^+ \rightarrow P.(Cr\ etc.)^\circ$$
I.E.P. raised

Example 3.

$$M = O;\ \bar{\nu} = O;$$
$$P.COO^- + (Cr\ etc.)^\circ \rightarrow P.(Cr\ etc.)^-$$
I.E.P. unchanged

Example 4.

$$M = O\ \bar{\nu} = -1;$$
$$P.COO^- + (Cr\ etc.)^- \rightarrow P.(Cr\ etc.)^=$$
I.E.P. lowered.

The above derivation is based on the assumption that complex bound acid proups are not affected by tannage. Normally, however, complex bound sulphate tends to become ionic during tanning and washing, thereby making the charge more positive, but on drying or dehydration the ionic sulphate groups tend to enter the complex, thus making the charge more negative, as found by Neal [8] and Otto [6]. The entry of complex forming anions of buffer salts into the collagen bound chromium will obviously have the effect of making the charge more negative.

Gustavson (loc. cit.) has made the point that the proportion of uncharged NH_2 groups at the pH of normal tannage is negligible, so that the amino groups of the side chains must be excluded from chrome tannage under normal pH conditions. On the other hand, however, we cannot agree with his suggestion that the hydroxy groups of hydroxyproline and serine are capable of coordinating to chromium under these pH conditions. Even the aromatic hydroxy groups, which are quite strongly electron donating, do not coordinate appreciably unless a five membered ring is possible, and Gustavson's comparison between collagen chain hydroxy proline and free glycollic acid does not seem to be sound. No evidence can be found in favour of coordination to chromium of the collagen hydroxy proline and serine OH groups under the pH conditions of normal chrome tanning.

Summary and Conclusions

The general equation is given for the influence of chrome tannage on the isoelectric point of collagen, and it is shown that the isoelectric point may be raised or lowered according to the charge on the resulting chromium complex coordinated to the protein carboxy groups. The effects of washing, drying and complex forming buffers are explained. Gustavson's conclusion that, under the pH conditions of chrome tannage, the amino groups of the side chains do not coordinate to chromium, is supported, but his suggestion that the hydroxy groups of hydroxy proline and serine can coordinate, is considered to be unsound.

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Received July 20, 1952

ABSTRACTS

The Stability on Storage of Leathers Tanned with Replacement Syntans and With Lignosulfonate Extracts. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.*, No. 3, 44-56 (1950). Commercial leathers that had been tanned with natural vegetable tannins exclusively (Type I), with admixture of 15 to 50 per cent of replacement syntans (Type II), or with admixture of 20 to 30 per cent of lignosulfonate extracts (Type III) were stored under normal warehouse conditions for 5 to 11 years. The leathers were analyzed, and tested for tensile strength at intervals. All types showed a progressive decrease in matter extractable with petrolic ether, in H_2O – soluble matter, and in pH value, and a progressive increase in degree of tannage and in difference figure. pH values were still over 3.8 and difference figures under 0.6 at the end of the tests. Types I and II showed no appreciable loss in tensile strength after 7.5 to 10 years (sole leather), 7.5 to 11 years (vegetable upper), 10 to 10.5 years (belting), or 8 years (harness). Type III leathers (sole and vegetable upper) lost 10 to 20 per cent of their initial tensile strengths in 5 to 6 years. There was no correlation between deterioration and increase in acidity.

H. B. M.

Diffusion and Binding of Synthetic Replacement Syntans. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.*, No. 1, 5-18 (1959). Laboratory tanning tests were made with 24 commercial (German) replacement syntans, using pieces of dehaired, delimed cattle hide. The tan liquors were strengthened gradually from 0.5 to 6.0 per cent tannin during 4 weeks, and the tannage was continued for 16 weeks in all. Tanning was done at the natural pH values of the syntans. Rate of diffusion was studied by making cuttings at 1, 2, 4, 6, 10 and 16 weeks and measuring depth of penetration. Time for complete penetration varied from less than 4 to more than 16 weeks. Stather's rule for rate of penetration of vegetable tannins did not hold for these syntans (see THIS JOURNAL **29,** 392). Rate of fixation of tannin was determined by analyzing samples taken at 2, 4, 6, 10, and 16 weeks. For tanning periods of 4 to 10 weeks, rate of fixation can be expressed by the equation: $B = K \times \log 2t$ where B = degree of tannage, K is a constant characteristic of the individual syntan, and t = time (THIS JOURNAL, **31,** 234). Values for K varied from 21 to 47. Those syntans that penetrated most slowly generally gave low values for K, but those that penetrated most rapidly did not necessarily give high values for K. Degree of tannage after 16 weeks varied from 62 to 30. In general, highest degree of tannage at 16 weeks was shown by syntans that penetrated completely in 6 to 10 weeks; those that penetrated very rapidly (under 4 weeks) gave slightly lower values, and those that penetrated slowly (over 10 weeks) gave the lowest values for degree of tannage. Firmness of combination was studied by treating 10 g. portions of the leather (16 week tannages) with 125 ml. H_2O for 24 hours, removing 100 ml. for determination of dissolved matter, adding 100 ml. H_2O, and repeating the process daily for 28 days. The amounts extracted during the first few days varied with the tanning material, and increased with the concentration of soluble matter in the final tan liquor. After 7 to 10 extractions, the amounts extracted per day became almost constant (about 10 mg.) and varied little with the particular syntan. Tendency towards hydrolysis, expressed as $100 \times (a - b) / a$, where a and b are degrees of tannage for leathers extracted 14 and 28 times respectively, varied from 7 to 37. The individual syntans are evaluated according to the above characteristics. H. B. M.

Vegetable Tanning VI. A Review of the Effects of Salts in Vegetable Tanning. By D. Burton and J. M. Harrison. *J. Soc. Leather Trades' Chemists*, **36,** 68 (1952). Salts play an important part in all tannery processes. In 1903 Procter pointed out that the neu-

tral salts of weak acids had considerable influence in producing mellowness, citing as examples sodium acetate and sodium sulfite. He suggested that the cause was the reduction of astringency, which could be restored by addition of free acid. The fundamental difference, with regards to salts, between chrome and vegetable tanning is that the acids and salts react with the chrome tanning molecules. This is not, with minor exceptions, the case in vegetable tanning. Basic chrome liquors prepared from sodium bichromate all contain sulfates and chlorides. Salts of organic acids may be present, produced in the reduction of glucose or added after the reduction. The presence of salts of organic acids markedly affects the tanning properties of chrome liquor and the physical properties of the leather, such as fullness, softness, substance and tightness of grain. Vegetable tanning liquors contain an even greater variety of salts. They may occur as salts of copper, iron, aluminum, zinc, calcium, magnesium, sodium and potassium, the last four usually predominating. All have effect on the leather. Pre-treatment of collagen with salts greatly influences the irreversibly fixed tan content of leather. Oxalates, succinates tartrates and citrates raise the shrink temperature of collagen; while chlorides, and to a lesser extent sulfates, depress it. Lyotropic effects of salts can be exerted in the pH range of tanning and affect the structural cohesion of collagen fibers. It has been shown that the plumping of limed hides in tan liquors is determined by the pH value and the valency of the anions present. It is now thought that proteins combine with anions as well as with hydrogen ions. There is little salt concentration in hides used in chrome tanning, although some is carried forward if the hides are delimed with boric acid. In vegetable tanning the first reaction in the suspenders is the neutralization of any alkalinity still in the hide. If allowed to accumulate, salts so formed materially reduce tanning action. On the other hand the lessening of such salt, when the hides are delimed with boric acid, makes necessary the control of time and concentration in tanning. Quick tanning processes usually include removal of alkalinity before tanning. Possibly the use of titration control of acids present would be useful in chrome as well as in vegtable tanning. Plumping of hides depends upon the pH, minimum at about 4.5 and maximum at about 2.4 pH. However, extent of swelling also depends on kinds and concentrations of salts present. Penetration of tanning agents is most rapid at low pH in chrome tanning and at high pH in vegetable tanning. Fixation of tanning molecules is just the reverse. In both chrome and vegetable tanning astringency is a function of at least four factors: the condition of the pelt; the nature and size of the tanning particles: the concentrations and kinds of strong and weak acids present and the concentrations of the salts of weak and strong acids present. Both are mellowed by the addition of chlorides and sulfates but more especially the salts of weak acids except carbonates and bicarbonates. The use of masking salts such as tartrates, oxalates, citrates, lactates, formates and others is well known in chrome tanning. It is realized that the effects produced depend upon the amount added. The effects of salt additions on the size of chrome tanning particles varies. Sodium formate and sodium oxalate have been found to have no effect; but sodium sulfite and sulfate have been found to increase the size. In vegetable tanning small quantities of salts may have a peptizing action. Larger quantities readily salt out the largest molecules, which are assumed to have the greatest affinity for the pelt. In chrome tanning the rate of diffusion is so rapid that the effect of salts on diffusion is of little consequence. The general conclusion of many investigators is that the rate of diffusion of vegetable tanning materials into the pelt decreases as the non-tan content increases. But this does not prove that salts hinder penetration. Present researches indicate that chlorides, sulfates and formates increase the rate of mimosa diffusion. It is well known that sodium chloride and sodium sulfate lessen the uptake of chromium from liquors containing basic chromium sulfate and sodium sulfate. Other evidence indicates that pH is important in evaluating the effect of salts, a change of pH sometimes reversing the effect. It has been shown that the degree of tannage was reduced in mimosa liquor, freed of bases, by the addition of calcium chloride. Salts of

weak acids may cause more chrome fixation by pelts. It has been shown in chrome tanning that the amount of acid taken up by the pelts is increased when sodium chloride is added to basic sulfate liquor and decreased by addition of sodium sulfate. The effects on vegetable tanning are being studied. In chrome tanning a pelt can take up strong acid from a mixture of a weak acid and a salt of a strong acid. Present authors found a similar effect in vegvegetable tanning with mimosa liquor. Boiling tests should be carried out on neutralized chrome leather. In vegetable tanning the effect of acid on shrinkage temperature is being investigated. The conclusion has been drawn that the stability of chrome leahter to boiling test is reduced if the sulfate radical is replaced by a monovalent radical. Total salts determination has been widely used to control hot pitting under the belief that the effect of acids can be controlled by presence of a sufficient quantity of salts. One investigator concluded that the type of salt is as important as quantity. The final conclusion of the authors is that more work on the effects of salts is desirable. R. H. T.

Sole Leather Tannages in Mimosa Liquors Containing Salts of the Lyotrope Series. By H. Lee and H. G. Wollenberg. *J. Soc. Leather Trades' Chemists*, **36**, 79 (1952). If collagen reaches equilibrium with normal calcium chloride there is a shift in the isoelectric point and its shrinkage temperature, as compared to less lyotropic salts such as sodium sulfate, is decreased. Calcium chloride causes swelling in the isoelectric zone and has a peptizing action on collagen. With increasing concentration complete solution takes place. Calcium chloride increases formaldehyde fixation over the entire pH range. Potassium chloride also increases formaldehyde fixation but does not affect the isoelectric point and the product is more stable than that made in the presence of calcium chloride. Wollenberg showed that the plumping pressures of pelts become lower in the presence of salts, except sodium bromide, which has a specific effect of maintaining or increasing plumping pressures. Plumping of lyotropic salts at pH 5 and 5.5 is visible when little acid is present. Its effect at lower pH is influenced by the type of acid. Wollenberg, using hydrogen bromide, enhanced its effect. Bennett summed it thus. In the case of neutral salts the place in the lyotropic series is the predominant influence. In the case of acids or alkalis, the greater effect of the hydrions and hydroxylions is predominant, but the place in the lyotropic series is still important. The experiments described were performed in order to compare normal mimosa tannages with strong and weak lyotrope salts present. Comparative pieces of delimed hide were tanned with liquors commencing with 10 degree barkometer and salt level adjusted to 0.205 N with potassium sulfate. They were then further adjusted to 0.33 N with potassium sulfate, sodium bromide and calcium chloride respectively. Then each of these sets were brought to a pH of 3 with sulfuric, formic and citric acids, making nine tanning liquors in all. Tanning was carried out for 54 days in cold liquors gradually strengthened to 140 degrees barkometer. Any water lost by evaporation was made up. After 54 days the leathers were hotpitted 7 days at 100 degrees F. in the same liquors. Measurements of elastic properties, hardness, substance, shrinkage temperatures and tensile strength were made. Later three tannages were repeated at pH 4.5. In all cases pH was maintained by adding sufficient amounts of the specific acid used. It was found that less titratable acid was needed to maintain the pH with calcium chloride than when a less lyotropic salt, such as potassium sulfate, was added. Nevertheless, if the leathers were hotpitted, the effect of the liquors at pH 3 in the physical properties is greater in the presence of calcium chloride and a lower amount of acid than is obtained in the presence of potassium sulfate and a greater amount of acid. The differences between the leathers at pH 3 was much greater than at pH 4.5. The hardness of the leathers, while actually immersed in the hot pit liquor, was greater for the lyotrope salt. Lyotrope effects seemed to result in increased water bonding when the pelt is in the untanned condition. The authors express the suspicion that the hard,

flexible bend leather of old-fashioned tanning might have been due to not removing the calcium salts, which exert a lyotropic action. R. H. T.

The Drying of Collagen and Its Reabsorption of Water from Humid Atmospheres. By F. E. Humphreys. *J. Soc. Leather Trades' Chemists*, **36,** 90 (1952). The difficulty of drying damp proteins has long been recognized. In order to compare the amounts of water held by collagen after different tanning treatments, it was necessary to adopt a standard method of drying applicable to all samples. It seemed possible that moisture content obtained at 100 degrees C. or higher in the conventional manner might lead to misleading results. Yet drying at reduced pressure over a desiccant is too slow and freeze drying is too troublesome. First the effect of drying technique on apparent moisture content was studied. Hide powder, screened through 20 mesh, was soaked in sterile distilled water with several water changes for 2 days at 20 degrees C. It was then strained through sterile muslin and pressed at 40 pounds pressure for 24 hours, giving a powder with about 25 per cent moisture. This was dried in the following ways: in electric oven at 110 degrees C. without prior treatment; in a desiccator at 20 degrees C. over phosphorous pentoxide; over silica gel until the moisture fell below 15 per cent and then in an electric oven at 110 degrees C.; in an oven at 103 degrees C.; in a steam oven at 97 degrees C.; in a steam oven at 97 degrees C. at a reduced pressure of 60 mm. Hg.; in a special drying appaatus (shown in a figure) at 60 degrees C. and 60 mm. Hg. pressure. The special drying apparatus was arranged so that a slow stream of air at low pressure could be drawn over silica gel and over the sample in a drying chamber. Drying was continued until no fall in weight occurred in an 8 hour period. In most cases a slight gain took place during the last drying period. The anhydrous hide powder absorbed moisture readily, even in an atmosphere as low as 32 per cent R.H. Hence all weighing dishes had to be air-tight. It was found that drying in the electric oven at 110 degrees C. gave the greatest amount of weight loss. Drying at 97 degrees and 60 mm. gave the same loss although more slowly attained. This was also true if the hide powder was conditioned by bringing to equilibrium with air at 75 per cent R.H. or if the hide powder was soaked as described above before drying. Therefore it was concluded that drying in an oven at 110 degrees C. is a satisfactory method for drying collagen. It was found that the hide powder dried at 110 or 97 degrees (reduced pressure) absorbed less moisture from humid atmosphere than prior to drying or if dried at below 60 degrees C. The effect is more pronounced if the collagen is wet when placed in the oven than if previously conditioned at 75 per cent R.H. (about 20 per cent water) and cannot be ascribed to hysteresis. R. H. T.

The Effect of the Degree of Tannage on the Acid Binding Capacity of Vegetable Tanned Collagen. By K. H. Gustavson and M. Nestvold. *J. Soc. Leather Trades' Chemists*, **36,** 105 (1952). The acid binding capacity of vegetable tanned collagen is practically independent of degree of tannage when above 30. Data on leathers of degree of tannage below 30 has not been available. For this study collagen was tanned both directly and by the organic solvent method which permits uniform vertical tannage using small amounts of tannins. There is still disagreement as to the function of the basic protein groups in tanning, varying from the opinion formerly held that vegetable tannin fixation is governed exclusively by the basic protein groups to the claim that these groups have no participation in vegetable tanning. Those maintaining the latter belief claim that the acid binding capacity of collagen is not affected by its combination with vegetable tannins. In a first series hide powder, lightly tanned with mimosa, was washed just sufficiently to remove sorbed matter and others fully washed until all but irreversibly fixed tannins were removed

and compared with specimens of high degree tannage similarly washed. The irreversibly fixed tannins caused an average decrease in binding capacity of 15 per cent. The water soluble matter did not influence the acid binding. In a second series solvent tannages with varying strength of solutions of mimosa and quebracho, up to 23 gr. tanning per 100 ml. solution were carried out. In this case a constant rather small lowering of the hydrogen ion binding power of collagen is noted in degrees of tannage from 6 to 9. Apparently tannage from solvents gives leather of greater acid combining capacity than corresponding leather of ordinary tannage and similar tannage degree. In a study of the fixation of the phosphate anion by collagen, polymetaphosphoric acid was prepared in 0.1 N strength by cation exchange of sodium polymetaphosphate. Pieces of quebracho tanned pelt (solvent tannage) corresponding to 1.0 gr. collagen were shaken intermittently for 20 hours with 25 ml. of the acid. The results showed that the irreversibly fixed tannins adversely affected the binding of the metaphosphoric acid somewhat more than hydrochloric acid. Only about two-thirds of the total number of acidic groups of the polymetaphosphoric acid function because of steric hindrance. In the reverse action the uptake of tannins by collagen, with its basic groups completely blocked by means of polymetaphosphoric acid, is practically inhibited in the initial stage, probably because of the inactivation of the basic protein groups, which apparently form the main nuclei for the early fixation of vegetable tannins. R. H. T.

The Determination of Tricresyl Phosphate in Cellulose-Finished Leathers. By L. M. Hill. *J. Soc. Leather Trades' Chemists*, **36,** 113 (1952). The author found it necessary to determine the amount of tricresyl phosphate used as plasticizer in nitrocellulose finishes. The analysis is complicated by the small amount of tricresyl phosphate in the presence of a large quantity of protein. Extraction of the plasticizer is complicated by presence of oils and fats in the leather and finely ground pigments carried over by the extracting solvent. Presence of pigments means that the analysis must include removal of other elements which may interfere with precipitation or colorimetric methods. Extraction and gravimetric determination of phosphate was not possible because of interfering substances. Decomposition of organic phosphates by oxidizing agents and determination of the orthophosphate colorimetrically as molybdovanadophosphoric acid was found to give accurate, reproducible results. The phosphomolybdate method used is described in detail with data showing that the method gives results consistently high. The colorimetric method used was as published by Simmons and Robertson (*Analytical Chemistry*, **22,** 294 and 1177 (1950). The only modification was that samples of leather were digested with either the sulfuric-nitric-potassium nitrate mixture or the sulfuric-perchloric-nitric acid mixture. A blank was prepared from a leather disc so digested and substituted for Simmons and Robertson's "Solution B". The standard graph, prepared with known amounts of potassium dihydrogen phosphate and solutions B (leather blank), C (nitric acid: water 1:2), D (0.25 per cent ammonium vanadate in nitric acid-water) and E (5 per cent ammonium molybdate solution) was identical with that given by Simmons and Robertson. Briefly the method consists in taking an aliquot of the digested, filtered leather phosphate solution, adding 5 ml. each of solutions B, C, D and E, diluting to 50 ml., allowing to stand 10 min. for color development, measuring the absorption density of the yellow solution at 460 mμ on a Beckman model DU spectrophotometer and reading off the phosphorous content from the standard gaph. The molybdovanado colorimetric method is straight forward, rapid and gives more accurate results than any other method used. R. H. T.

A New Method for Determining the Flexing Properties of Vegetable Tanned Sole Leather. By P. J. Dwyer. *J. Soc. Leather Trades' Chemists*, **36,** 119 (1952). A simple method of measuring numerically the flexibility and rigidity (feel) of leather would

be of value to the tanner, buyer and research investigator. Many methods for determining flexibility, rigidity, firmness, etc., are known. In the U. S. A., Federal Specification No. K K-L-311 Method No. 250 describes the means of measuring the resisting force required for deflecting a leather sample clamped with jaws at one end. Other simple deflecting methods are listed. This paper describes an apparatus and method for determining flexibility while flexing at the rate of 30 to 40 flexes per minute. A picture, drawing and description of the apparatus are given. It consists essentially of a piece of leather, 2 in. by 2 in., clamped in fixed jaws at one end and to a pendulum at the opposite end with the result that the leather becomes an integral part of the pendulum. The pendulum is set swinging and the time required for it to reduce its arc between arbitrary limits measured. The leather tends to restore the pendulum to zero displacement. Mathematically this restoring force is proportional to the moment of inertia (I) over the time period (T^2) in seconds. The value I/T^2 is determined as a numerical measure of the flexibility. The method was used in an exploratory experiment on a bend of sole leather. The variation of the property was measured with respect to the orientation of the sample to the backbone and its position on the side. The samples were flexed dry and saturated wet after washing for four days in running water. The flexing properties of the wet leather show a relationship to the position of the samples in the side which is in agreement with the quality variation usually held in practice. The method confirms the accepted fact that leather is more flexible in the direction parallel to the backbone than perpendicular to it. As a means of following alteration in a physical property during tanning the method is ideal, in that the leather can be tested in the wet state and non-destructively. R. H. T.

Unhairing By Mans of Enzymes. By G. H. Green. *J. Soc. Leather Trades' Chemists*, **36,** 127 (1952). The author attempts to cover the literature in an orderly fashion, dividing the agents into animal, fungal bacterial, plant and miscellaneous proteases. The first successful animal proteases used were pancreatic enzymes eventually combined with caustic alkali, alkali earth or ammonium sulfate for the pretreatment with addition of a neutral salt, especially sodium sulfate, to prevent swelling. An investigation of the chemistry of the process brought the conclusion that the enzyme action involves merely the partial hydrolysis of the proteins binding the hair and epidermis to the underlying connective tissue. In another development sun dried goatskins, placed in 0.2 per cent pancreatin at pH 8 under toluene, unhaired easily after 14 days. Pretreatment of hides with 0.02–0.04 per cent pancreatin, while not loosening the hairs, shortened the liming by 20 hours. Other animal proteases which have been used are, cathepsin from animal liver and kidneys and the enzymes from fish entrails, preferably from carp. Pepsin was not found to be an unhairing agent. A claim has been made that an autolytic enzyme exists in skin which can itself cause hair loosening. Fungal proteases followed naturally because of similarity to pancreatin. Enzymes from the following molds have been used: A. niger, P. glaucum, Mucor mucedo, A. oryzae, A. flavus and A. parasiticus. The conditions under which most of these molds are made and used are described. Bacterial proteases are largely responsible for the effect of dog and hen dung, hence unhairing with these agents followed naturally. Other bacterial enzyme sources are: B. mycoides, megatherium and mesentericus, B. subtilis and liquifaciens, B. coli commune, Staph. pyogenes albus, B. sphaerivus, vulgatus and ochraecum. As with the animal proteases the various methods for their use are briefly described. It is claimed that the bacterial enzymic activity of a used soak liquor activitates unhairing with lime liquor 100 fold. The only plant protease which has been studied in detail for unhairing is papain. Several methods for its use have been tried. Stiasmy claimed that it is useless for unhairing because it attacks collagen more readily than the Malpighian layer. Under miscellaneous, combinations of mold, bacterial and animal proteases are described as having been used.

One patent uses a combination of any proteolytic enzyme and a C_2–C_8 aliphatic amine with a phenol antiseptic. There are 61 references. R. H. T.

Energy and Entropy Effects on the Elasticity of Collagen Fibers. By R. H. Hall. *J. Soc. Leather Trades' Chemists*, **36,** 137 (1952). Two mechanisms exist which can cause materials to exhibit elasticity. They are deformation of atomic bonds, as in metals at low extensions, and the alignment of molecular chains on stretching, with resulting entropy decrease, as in rubber. In the latter case removal of the stretching force produces a tendency to increase the entropy and the thermal motion of the chains causes the material to contract. The purpose of this work is to examine the energy-entropy relationship in collagen at various extensions, by means of the Wiegand-Snyder equation, based on thermodynamic reasoning. The derivation of the Wiegand-Snyder equation, dividing stress in a deformed material into energy and entropy components, is described. Experiments involving the application of this equation to skin collagen fibers were carried out and showed that the elasticity of the collagen fibers at pH 7 in water is due to internal energy changes, but that rubber-like elasticity with decrease in entropy on stretching is displayed when the fiber is swollen in hydrochloric acid at pH 1.75. After liming, it was found that a slightly greater expenditure of energy was required to deform the fiber by a given amount. It is suggested that this may be due to the establishmentof additional salt links by carboxyl groups produced by hydrolysis of amide groups during liming. Values are given for the coefficients of linear thermal expansion of collagen under various conditions. R. H. T.

Tannins IV. The Complexity of Tannin Extract Composition. By T. White, K. S. Kirby and E. Knowles. *J. Soc. Leather Trades' Chemists*, **36,** 148 (1952). This is a continuation of a study, begun 5 years ago, of mimosa and quebracho extracts bringing up to date the results obtained with improved methods. Publications quite generally have inferred that extracts of tanning agents can be purified to a single characteristic tannin. This is true more for catechol tannins than for pyrogallol tannins which are more often recognized as complex. The authors maintain that practically all the so-called purified extracts examined to date have really been complex mixtures and that, if an individual tannin is segregated and purified, it is not valid to consider it as representing the effective tanning agency of the extract. The fact that there are usually several polyphenolic tannins in a single extract and that these are often mutually solubilizing, brings about considerable difficulty in separation. For example, isolated fractions may not dissolve in the solvent which dissolved the original extract; or isolated fractions may be readily soluble in solvents which will not dissolve them out of the original extract. Remarks in this paper are confined to the method of fractionation by distribution between immiscible solvents. A typical counter current extraction of mimosa extract with ethyl acetate and water in 9 steps is described, resulting in 9 fractions each of acetate and water layers. These were evaporated to dryness, giving the following percentages of the initial extract: 1–3.75, 2–5.09, 3–5.17, 4–5.48, 5–5.80, 6–6.04, 7–5.92, 8–6.54, 9–56.86. Chromatograms of fractions 1, 3, 5, 6, 8 and 9 were taken as representative. Eighteen photographs of these were taken. The series demonstrates the complexity of the extract. The authors believe that, as the phenolic tannins are combined with the hide, their solubilizing action is removed and fractions, previously soluble, are deposited in insoluble form, thus appearing as fixed tans, although not actually combined with the hide. In the case of mimosa extract, the insoluble sludge deposited in the tan pits can be identified chromatographically as part of the fraction 9 mentioned above. A normal mimosa extract contains some 76 per cent of tannin by official hide powder method; but, when fractioned and the tan content of the fractions determined in the same way, they add up to show about

66 per cent of the original tan now showing up as non tans. In other words the original analysis was high because non tans were deposited as insolubles which are not washed out. This, as the authors point out, brings up the question as to what are tans and what non tans, it being possible for a substance to be either tan or non tan, depending upon the method of analysis. Apart from any such controversial question the authors have demonstrated the need of considering the complexity of tannin extracts. R. H. T.

Physical and Physico-Chemical Constants of Leather and Collagen. By C. E. Weir. *J. Soc. Leather Trades' Chemists*, **36,** 155 (1952). The physical and related physico-chemical properties of leather and collagen as made at the U. S. National Bureau of Standards are reviewed. A table shows the real and apparent densities of 5 types of leather. A figure showing temperatures vs. increase in volume curves for 7 leathers with a brief discussion covers expansivity. Shrinkage studies, based on the effect of 16 tanning agents on kangaroo tail tendon collagen, are discussed. The general conclusion is that shrinkage of collagen involves rupture of hydrogen bonds alone. Compressibility studies in the range of 2,000 to 10,000 atmospheres have been made showing a decrease of about 10 per cent in real volume at the highest pressure. This places leather in comprssibility with the high polymers, lower than true liquids but higher than solids. Measurements of Poisson's ratio have shown that the real value is 0.50. Attempts to measure the apparent value of Poisson's ratio were unsuccessful. Real dielectric constants, measured on the dry leather, are: tendon collagen 5.1, chrome leather 5.4 and vegetable leather 6.3. Direct current resistance measurements carried out at 23 degrees C. showed that the resistance decreased from extremely high values ($< 10^{14}$ ohms) in dry leather to values of the order of 1×10^{6} ohms at moisture content of 15-20 per cent of water. Figures are given showing curves of water adsorbed against relative humidity. Chrome leather and hide powder exhibit the greatest adsorption capacity. With increasing temperature the adsorption capacity decreases. From the high values of the heat adsorption (13,000-16,000 cal/mol) at low moisture contents, it is concluded that hydrogen bonding between water vapor and either excess carboxyl groups or ions in the collagen of leather is responsible for the initial adsorption. Calculations made on adsorption data show that the available surface area of leather may vary between 250 and 350 m^2/gram of leather. R. H. T.

Improved Ferric Chloride Test for Phenols. *Analytical Chemistry*, **24,** 979 (1952). The test for phenols, consisting in the treatment of the unknown in water, ethanol or methanol solution with ferric chloride in the same solvent, fails to give a positive test with many phenols. Examples are p-benzylphenol, meso-hexestrol, trans-diethylstilbestrol and ethyl p-hydroxybenxoate. It was found that the presence of pyridine so improved the test that nearly all phenols gave colors. Exceptions are phenolic carboxylic acids, in which the carboxyl competes with the hydroxyl, and a few cases of steric hindrance. Solvents used were water, methanol, chloroform and diethylene glycol diethyl ether. A table shows the color tests of 78 phenols in these four solvents. Directions for making all solutions and procedure of the test are given. The effect of variation of solvents is described and the chemistry involved in the test discussed. R. H. T.

Problems of the Leather Industry in Slovenia. By I. Vizovisek. *Nova Proizvodnja*. No. 3, 191 (1952). The productive capacity of the Slovenia leather industry comprises not less than 48 per cent of Yugoslavia's capacity. In spite of the more advanced organization

of hide buying and collecting in Slovenia (3 kg. per inhabitant), only 18 per cent of the hides for disposal on the markets in Yugoslavia reach the plants in Slovenia. If Slovenia's method of hide collection were extended to all Yugoslavia, there would be an excess of hides equivalent to 20 per cent above the requirements of all Yugoslav tanneries. In Slovenia there are 6 specialized, 3 major and some minor tanneries. Two new tanneries have been erected recently. Modernization of the remaining plants is necessary. Many of the chemicals required in tanning have to be imported. The leather industry lacks specialized technicians and these are essential if leather quality is to be improved. An association of tanners and shoe manufacturers has been formed to promote professional training and instruction with the object of overcoming the foregoing deficiency in skilled personnel.

Activation of Hydrolytic Lignin by Various Methods. By N. G. Mendlina. *Zhur. Priklad. Khim.* **24,** 640 (1951). Through *Chem. Abstr.* **46,** 733 (1952). Hydrolytic lignin, obtained by treatment of cellulose matter with dilute mineral acids under pressure at high temperature, is almost completely insoluble and has few OH groups. Treatment with sulfites, bisulfites, free sulfurous acid, or chlorination does not yield soluble products. Treatment with 10 per cent oleum gives about 50 per cent soluble matter which, upon treatment with $CaCO_3$, displays tanning properties. Treatment of the lignin with phenol (6-12 hours) gives a condensation product that is insoluble in water, but subsequent sulfonation, as above, gives a completely soluble product suitable for tanning and of somewhat better quality than cellulose-sulfite extracts. The sulfonation is best done with 200 per cent oleum (with respect to product by weight) for 5 hours at 25-80°.

Increase of Permeability of Unhaired Skin Upon Dehydration. By P. Y. Frenkel and A. H. Mikhailov. *Legkaya Prom.* **11,** No. 6, 45 (1951). Through *Chem. Abstr.* **46,** 767 (1952). Flow of liquid through unhaired skin treated with dehydrating salts or pickling solution, as determined with the aid of the Poiseille equation for flow through capillaries, indicates that flow is chiefly through pores having a radius of 1-20 μ. Pores with a radius greater than 1 μ are absent in unhaired skins swollen with water.

Optimum Conditions of Using Spruce Extract. By M. Z. Gelfgat. *Legkaya Prom.* **11,** No. 4, 32 (1951). Through *Chem. Abstr.* **46,** 767 (1952). In chrome-vegetable tanning of hard leathers, optimum conditions for use of spruce extract are: pH 4.7 - 5.0 and 4.0 - 4.4, temperature 20-30° and 43-48°, liquid coefficient 1.6 - 1.8, and 1.4 - 1.6, and duration 12-16 and 36-40 hours in first and second phases respectively. Maximum allowable amount of syntan AN and sulfite cellulose extract is 20 per cent. The leather was clear, of good appearance, and had a high degree of tannage.

The Manufacture of Synthetic Tanning Agents. By G. Toth. *Magyar Kem. Lapja* **5,** 231 (1950). Through *Chem. Abstr.* **46,** 767 (1952). A detailed summary with 46 references.

Emulsifying Paste for Fatliquoring Leather. By S. V. Arbuzov and I. N. Veretennikov. *Legkaya Prom.* **11,** No. 5, 38 (1951). Through *Chem. Abstr.* **46,** 767 (1952). The paste, prepared from saponfied synthetic fatty acids in oxidation of petroleum, gives suffi-

ciently stable emulsions with all liquid fats used in leather manufacture, with solid fats, and paraffin. A 2 per cent emulsion has a pH of 7.4-8 - 8.0. Fatliquoring with the above paste and in combination with other fats had no harmful effect on leather and did not lower adhesion of films to leather. The paste is more economical than sulfated fish oil. Compositions of mixtures for various leathers are given.

Effect of Water Soluble Substances Upon the Physico-Mechanical Characteristics of Leather. By G. I. Kutyanin. *Legkaya Prom.* **11,** No. 5, 42 (1951). Through *Chem. Abstr.* **46,** 767 (1952). In vegetable tanned leather, with increasing intensity of washing, there was a decrease of total amount of tannins and along with it, deformation under compression increased and yield of dry leather decreased. There was a direct relationship between resistance to compression and tannin content; however, an excess of unfixed tannins increases only the hardness of the leather and not the intermolecular reaction of the structural elements of the collagen. Relative changes in deformation under compression and increase in shrink temperature after removal of the water soluble substances were insignificant. Apparent volume of skin and its thickness in the wet state were somewhat increased after tanning. Removal of the water soluble substances had practically no effect on the volume, thickness, and area of the wet leather, but after drying, these showed a decrease.

Thermostable Insole Leather for Hot Vulcanized Footwear. By N. B. Brodetskii, T. P. Zemzer and I. G. Maslov. *Legkaya Prom.* **11,** No. 7, 28 (1951). Through *Chem. Abstr.* **46,** 768 (1952). Soaking, liming, pickling, and chroming procedures are as usual. Three stage vegetable retanning is employed, with one of the following compounds: oak 80 + AN 20, oak 60 + AN 20 + PL 20, oak 30 + spruce 30 + AN 20 + PL 20 per cent. Chrome content in leather was kept at 1.5 - 1.7 per cent (for 0.0 moisture). AN and PL are syntans.

The Resistance of Sole Leather of Different Tannages Towards Water. By W. Weber (Eidg. Materialprufungs und Versuchanstalt Ind., Bauwesen u.Gewerbe, St. Gallen, Switz.). *Festschr. Paul Schlapfer,* 191 (1950). The water proofness of various leathers tested increased with the sp.gr. of the leather and with the content of water soluble material up to a certain value. The water absorptive power and the water proofness also depended on the mechanical treatment, the structure of the leather, and the type of tanning.

Controlling Lacquer Coating for Leather. By S. A. Kuraitis. *Legkaya Prom.* **11,** 35 (1951). Through *Chem. Abstr.* **46,** 768 (1952). Sp.gr. is not a good index of suitability of lacquer; viscosity is a better index. Optimum thickness is 0.60 - 0.07 mm. Lacquer shouldshould be diluted to a viscosity of 1 second (determined with the aid of a falling ball weighing 2.09 g.) and should be spread so that 130 g. will cover 1 sq.m. of leather.

Effective Method of Evaluating Interaction of Collagen with Electrolytes. Fy O. V. Matvuva and A. N. Mikhailov. *Legkaya Prom.* **11,** No. 7, 34 (1951). Through *Chem. Abstr.* **46,** 768 (1952). Reaction between unhaired skin and electrolytes was studied by determining the membrane potential of the skin. A strip of unhaired skin and an equilibrium solution of electrolyte were joined with two identical calomel electrodes as fol:

lows: calomel electrode: saturated KCl: skin: equilibrium solution of electrolyte: saturated KCl: calomel electrode. After determining the membrane potential and the concentration of H^+ in the equilibrium solution, the concentration of H^+ in the skin was calculated from $E = 58 \log^{x}/_{y}$, where $\log^{x}$ is pH of the water solution and $\log_y$ is the pH of the skin. The addition of neutral salt did not result in complete equalization of the concentrations of the diffusing ions; this was determined also by direct measurement of pH within the skin by means of an Sb electrode. Potentials of skin treated with various salts indicate that the magnitude and nature of the charge can be used to evaluate the relative absorptions of one of the ions of the neutral salt. On this basis, sulfates of NH_4, Na, and Mg, NH_4CNS and NH_4NO_3, and Na_2CO_3 and $NaNO_3$ are anionphilic while $CaCl_2$ and $BaCl_2$ and $Cr(SO_4)_3$ and $Al_2(SO_4)_3$ are cationphilic. For some salts, the predominant absorption of cation or anion depends upon concentration of the salt; NaCl and LiCl are anionphilic at low concentrations and cationphilic at higher concentrations while NaOAc changes from cationphilic into anionphilic with increasing concentrations.

Canaigre—A Desert Source of Tannin. By A. Krochmal and S. Paur (Cornell Univ., Ithaca, N. Y.) *Economic Botany* **5,** 367 (1951). Through *Chem. Abstr.* **46,** 1277 (1952). A review of work on *Rumex hymenosepalus.*

Displacement of Sulfate Groups in Chromium Complexes by Functional Groups of Cation Exchangers. By K. H. Gustavson (Garverinaringens Forskingsiust, Stockholm). *Svensk Kem.Tid.* **63,** 167 (1951). Through *Chem. Abstr.* **46,** 1280 (1952). Analyses of aged dilute solutions of $Cr_2(OH)_2(SO_4)_2$ (total Cr in cationic form) by means of ion exchangers suggest that the sulfate groups are present as a bridge between 2 Cr atoms or attached to one Cr atom (less stable). The cationic complexes fixed by a sulfonic acid type exchanger contained 1 sulfate *I* group on 4 Cr atoms, that is, about half of the complexly bound *I* was displaced in the interaction with the resin. A cationic exchanger of the carboxylic acid type displaced about 75 per cent of the complexly *I*, showing the power of the CO_2H group of the resin for complex formation. The CO_2H groups of collagen did not remove any *I* groups in their attachment of cationic Cr. When ionic *I* was removed with anionic exchanger, the resulting solution contained cationic Cr complexes with one *I* group per Cr atoms (33 per cent acid sulfate Cr complexes). The Cr complexes fixed by collagen showed a similar ratio of *I* groups to Cr, after removal of protein-bound *I* with pyridine.

Analysis of Waste Waters from Tanneries. By I. Buckmans and P. Beaujean. *Bull. cestre belge etude et document. eaux.* (Liege) No. 7, 443 (1950 **1**). Through *Chem. Abstr.* **46,** 1678 (1952). A study of toxic effect on fish and possible purification methods for waste liquors from various steps of tanning operations. The work is concerned with (1) establishing the principal characteristics of the crude liquors, e.g., color, odor, turbidity, pH, suspended matter, and concentration of predominant toxic compounds, (2) giving an outline of treatment methods for either the crude or decanted liquor, and (3) determining the toxic effect of all crude and treated waters on fish. Results are presented in tabular form and classified according to types of liquor resulting from the different operations.

Toxicological Tests of Certain Products Used in Tanning. By E. Leclerc and F. Devlaminck. *Bull. centre belge etude et document. eaux* (Liege). No. 9, 541 (1950 **111**).

Through *Chem. Abstr.* **46,** 1679 (1952). Fatal doses for minnows *(Phoxinus laevis)* were determined for (1) free mineral and organic acids, (2) mineral salts of a strong base, (3) special salts such as oxidizing, reducing or antiseptic, and (4) hemoglobin poisons. Detailed tables are given for HCl, H_3BO_3 and tannic and lactic acids.

Determination of Calcium and Magnesium in Limestones and Dolomites. By J. J. Banewicz and C. T. Kennen (Southern Methodist Univ., Dallas, Texas). *Anal. Chem.*, **24,** 1186 (1952). The method of Schwartzenbach for the determination of the sum of calcium and magnesium in water using ethylenediaminetetraacetic acid (Versene) as the reagent and Eriochrome Schwartz T as an indicator, was examined further for the determination of both calcium and magnesium. The sum of the two constituents was determined by the foregoing method, the calcium precipitated by two different methods, and the magnesium titrated by Versene method. Analysis of Bureau of Standards samples were in very close agreement with the known composition. Directions are given for overcoming the interference of iron and alumina on the titration end point when these materials are present in excess.

The Mixing of Casein Glues. By P. M. C. Lacey. *J. Appl. Chem.* **2,** 408 (1952). In the mixing of prepared casein glues with water in quantity, the difficulties met with, namely: lump-formation and air-entrainment, arise from difficulties experienced by the particles in penetrating the water surface, especially if the water already has part of the casein dissolved in it. It is shown that the mixing problem can be solved by carrying out the operation on a continuous basis, and using centrifugal forces to submerge the particles; a machine has been built in which correctly proportioned streams of casein powder and water are passed into a specially designed centrifuge cup, continuously discharged at the top through a scoop-tube; a scraper provides reflux near the base, and air is removed centripetally as the materials ascend the divergent walls. The machine absorbed only 1/15 h.p. and yielded a virtually faultless mix at rates up to 20 lb. per minute.

Two Dimensional Paper Chromatography of Proteins. By H. Tauber and E. L. Petit. (Univ. of North Carolina, Chapel Hill, N. C.). *J. Amer. Chem. Soc.*, **74,** 2865 (1952). A protein staining agent, containing the movement of proteins in two-dimensional filter paper chromatography. Improvements in the two-dimensional technique are described.

The Reaction of Brom Phenol Blue With Amino Acids and Peptides. By I. I. Geschwind and C. H. Li. (Univ. of Cal., Berkeley). *J. Amer. Chem. Soc.*, **74,** 834 (1952). Brom phenol blue affords a sensitive indication of the presence of proteins in paper electrophoresis. The paper is dipped in a 0.1 - 1 per cent solution of the dye in ethanol saturated with $HgCl_2$. Rinsing the strip in water, with or without prior fixation, allows the removal of excess dye, leaving the protein-containing areas a green-blue color. Of the naturally occurring amino acids studied histidine gave a definite positive reaction. Glutathione also gave a positive reaction. It was also found that if the chromatograms were treated very quickly with NH_3 vapor prior to the application of the dye, after the final washing with water, arginine, histidine, lysine and histamine showed up as royal blue spots on a light blue background.

The Application of Newer Electrical Measuring Techniques in the Tannery Laboratory. By H. Ebert. *Das Leder* **2,** 213 (1951). A lecture. The electrical effects can be divided into the following two groups of 4 subgroups each: I Electrical energy is amplified; (1) EMF measurements (redox potentials and concentration cells), (2) change of light energy to electrical (spectrophotometry), (3) change of mechanical energy to electrical (piezoelectricity), (4) change of heat energy to electrical. II. The system modifies electricity supplied from an outside source; (1) low and high frequency conductivity (conductrometric titrations), (2) measurements of dielectric constant, (3) fractionation in an electric current (electrophoresis), (4) measurement of oxidation-reduction potential at a dropping mercury electrode (polarography). I. D. C.

The Titrimetric Determination of Calcium and Magnesium with Komplexon. By O. Engel. *Das Leder* **2,** 241 (1951). Spiers *(J.S.L.T.C.* **34,** 289) has investigated a Komplexon method for determining magnesium in leather ash. Komplexon, disodium salt of ethylene-diamine-tetra-acetic acid, and Murexid, ammonium salt of purpuric acid, can be obtained from G. Jacoby, Hamburg. If metal cations form stable complexes with the carboxyl groups of Komplexon, acid is liberated and may be titrated either with alkali or by the iodide-iodate method. Another possibility is to use two complex-active organic compounds, one of which acts as an indicator by changing color when it combines with the metal cation. To titrate magnesium alone, the solution must contain not more than 0.2 grams magnesium per liter. To 100 cc. of solution add 5 ml. of buffer (350 ml. of 25 per cent ammonia and 54 grams ammonium chloride per liter) and 10 drops of Eriochrome Black T solution (2 grams in 500 ml. alcohol), then titrate at not below 40° with the Komplexon solution, (37.12 grams per liter; 1 ml. = 2.432 milligrams magnesium). The color change is from wine red to blue. For calcium determination the solution must not contain more than 0.5 grams calcium per liter. Add sodium hydroxide to keep the pH above 12. Add saturated aqueous Murexid solution to form a deep red solution then titrate with Komplexon to a blue violet. One ml. of 0.1 molar Komplexon solution is equivalent to 4.008 milligrams calcium. Only calcium is determined by the Murexid method. If magnesium is to be determined in a solution containing calcium, the latter may be removed as oxalate or both calcium and magnesium may be determined by the eriochrome black method then calcium may be determined and subtracted from the total. I. D. C.

New Uses for the Combination Tannage with Chromium and Aluminum Salts. By G. Otto. *Das Leder* **2,** 281 (1951). Combined tanning with chromium and aluminum is not new. One type is that in which an alum pickle precedes chrome tanning, another is that in which a chrome retannage is used to render alum tanned glove leather washable. The combination tannage, however, has disadvantages as well as advantages. If the alum is used first, the leather has a firm grain but is somewhat flat. The first tannage combines with the most reactive groups and largely determines the character of the leather. There is a possibility, however, that the second tanning material may combine with the first which is already fixed in the skin. To investigate this matter, portions of a suspension of electrolyte-free chromium hydroxide were treated with increasing amounts of a solution of aluminum chloride (Blancotan B, containing 2.5 per cent Al_2O_3). The pH values of these solutions were lower than those of corresponding aluminum chloride solutions without chromium hydroxide. This can only be explained by absorption of a basic aluminum compound by the chromium hydroxide leaving aluminum chloride of lower bacicity in solution. Also less aluminum than expected was found in solution; approximately one-third was removed from

solutions containing one-half as much aluminum salt as chromium hydroxide and up to two-thirds for lower proportions of aluminum. The chromium compounds in freshly tanned chrome leather should react in a similar manner with basic aluminum chloride solutions, and this would explain the favorable plumping and tightening action of an alum retannage. The use of aluminum salts is disadvantageous because aluminum forms water repellent compounds with free fatty acids. Fatliquors for leather tanned with aluminum salts must not contain soaps or free fatty acids, otherwise the leather surface will repel water so that it can not be wet back and dyeing and finishing will be difficult. Also the fatliquor does not penetrate well and the leather is stiff. Anionic dyes do not penetrate well if the leather is tanned with aluminum compounds. A comparative test disclosed that aluminum hydroxide took up anionic dyes and turkey red oil more completely than did chromium hydroxide. Fat liquor penetrates dyed leather better than undyed because the reactive groups on the surface have been satisfied by the dye. Fatliquoring difficulties can also be avoided if the leather is treated before, after, or instead of dyeing, with a few per cent of gambier, or a gambier substitute, Tamol GA. Suede leather requires a dense fiber structure. This can be obtained by retanning with unmasked chrome liquors, but such leather contains 9-10 per cent Cr_2O_3 and has low tensile strength. Retannage with basic aluminum compounds does not lower strength and the absorption of dye is improved. Oils which have been made water soluble by introduction of sulfo or carboxyl groups, as are most commercial oils, are not suitable for preoiling chrome or combination tanned suede leather. These anionic oils prevent take up of other anionic substances to such an extent that saturated color tones can not be produced. These difficulties can be avoided by use of the recently developed cationic fatliquors. I. D. C.

The Behavior of Fat Replacement Materials in Stuffing Vegetable-Ttanned Leather. By H. Herfeld and R. Lauffmann. *Ges. Abhandl. deut. Ledernists. Freiberg/Sa.* No. 2, 52 (1949); cf. Stather and Schubert, *This Jour.*, **33,** 444 (1938). Work previously done with natural fats and greases is extended to 16 synthetic replacement fats. These are described as replacements for fish oil, tallow, and neatsfoot oil. They included Derminolöl Nos. 1, 2, and 3, Derminol Narbenöl, Derminolfett Nos. 1, 2, and 3, Derminol Degras, Lederöl Nos. S215, 1215, and 111, Lederfett GL320, Lickeröl KL conc., Degoran, Montan-Lederfett, and Penreco WTHS 9532. Composition of these materials is described very sketchily (see Brown *et al*, THIS JOURNAL, **46,** 483-527 (1951). Analytical characteristics are tabulated. "Pure fat" (non-volatile matter soluble in CCl_4) varied from 79 to 98 per cent, most of the balance being matter volatilized in 5 hr. at 100°; I_2 No. varied from 0 to 118, and Acid No. from 0.3to 34. The general plan was to treat 10 g. of sand, heavily tanned hide powder, lightly tanned hide powder, or untanned hide powder, with replacement fat containing 1.5 g. of "pure fat" dissolved in ether. The ether was allowed to evaporate, and the fat was extracted from the sand, leather or hide powder with CCl_4. This was done immediately, after aging for 3 days and for 4 months at 20°, and after aging for 3 days and for 4 weeks at 40°C. The fatty matter recovered was calculated as percentage *(E)* of pure fat. I_2 No. and Acid No. were determined for each extract, and compared with the starting material. For sand, not aged, *E* was 90 to 97 for all materials except Derminol Degras 1 (87) and Lickeröl KL conc. (76). For one group of compounds that included Derminolöl Nos. 1 and 3, Derminolnarbenöl, Derminolfett Nos. 1, 2, and 3, Degoran, and Lickeröl KL conc., *E* was the same for sand, and for fully tanned, lightly tanned and untanned hide powder, and did not change on aging. For the remaining materials, the value of *E* before aging declined in the order: sand, heavily tanned hide powder, lightly tanned hide powder, untanned hide powder. For this group, *E* declined with aging time and especially with

increasing aging temperature; aging for 3 days at 40° brought about the same decrease in *E* as aging for 4 months at 20°. The change of *E* on aging was as great, or greater, for aging on sand as for aging on tanned or untanned collagen. This is illustrated by the following data:

	% of given fat extractable with CCl_4 (E)							
	From sand		From hide powder					
			heavily tanned		lightly tanned		untanned	
Material	not aged	aged 4 weeks at 40°	not aged	aged 4 weeks at 40°	not aged	aged 4 weeks at 40°	not aged	aged 4 weeks at 40°
Derminöl 2	93.4	90.2	91.5	89.1	90.7	86.5	90.1	84.6
Derminoldegras 1	86.8	79.1	85.0	78.5	83.3	78.3	82.6	77.2
Lederöl S 215	94.2	87.3	92.8	86.8	92.4	83.7	89.9	82.9
Lederfett GL 320	95.2	90.8	94.5	88.2	93.8	87.2	91.5	86.0
Lederöl 111	96.5	86.1	93.4	84.1	89.3	83.1	87.4	81.8

The lower extractability of the fats from hide powder, compared to sand, before aging, is believed to indicate some combination between fatlike material and collagen. There was no relationship between initial I_2 No. or Acid No. and decrease in *E*. Most, but not all, I_2 Nos. of the extracted fats decreased on aging, but there was no relation between decrease in I_2 No. and decrease in *E*. I_2 Nos. decreased a little more on hide powder, tanned or not tanned, than on sand. Acid Nos. increased on aging in nearly all cases. In some cases the increase of Acid No. was greater on sand than on hide powder (tanned or not tanned), which the authors interpret as meaning that the acid constituents are fixed by collagen. These changes in I_2 No. and Acid No. are mostly quite small. The tannage was done with chestnut extract to give degrees of tannage of 39 and 63 for the lightly tanned and heavily tanned hide powders. H. B. M.

The Behavior of Fat Replacement Materials in Fat-Liquoring Chrome Leather. By H. Herfeld and R. Lauffmann. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 1, 72-83 (1949); cf. Stather and Herfeld (THIS JOUR. **28,** 173, 372 (1933). The work previously done with natural fats was repeated, using 11 replacement fats, of widely different composition, all of which are said to have been used successfully for complete replacement of natural fats. These were: (1) *Mersolate*, a Na salt of sulfo-acids obtained by treating straight chain hydrocarbons, 15-18 C, with SO_2Cl_2 or chlorsulfonic acid; (2) *Derminol Licker L*, a mixture of the Na salt of a high molecular weight carboxylic acid, containing N and S, with unaltered hydrocarbons, (3) *Derminol Licker P*, an emulsifiable mixture of mineral oil with a high proportion of anionic emulsifying agent; (4) *Essatol WL*, a sulfonation product of synthetic esters containing fat acids with 4-11 C and alcohols with 6-14 C; (5) *Essatol RS*, a mixture of No. 4 with a high proportion of unsulfonated ester and a little sulfonated alcohol; (6) *Es-Te-Licker BS*, a mixture of mineral oil, "aromatic compounds," and Na salts of aliphatic sulfo-acids; (7) *Eucoriol NS*, an emulsion of hydrocarbons, not further described; (8) *Adolite F*, a stabilized mixture of mineral oil with condensation products of fat acids and high molecular weight protein decomposition products; (9) *Lickerol KL conc.*, a mixture of mineral oil and vegetable oil sulfonates; (10) *Geladol S 42*, an NH_4 salt of an acid, containing S, derived from Mersol; (11) *Geledol S 42 AO*, same as No. 10 acidified with HCOOH. Nos. 1, 10 and 11 are fully soluble in H_2O; the others give stable emulsions (No. 9 least stable). Analytical characteristics are tabulated. For comparison, tests were made also with 2 commercial sulfated fish oils of low degree of sulfation

(12) and high degree of sulfation (13). Tests were made by shaking chrome-tanned hide powder (containing 5 g. collagen) with a known wt. of "pure fat," usually 0.25 g., in a definite volume, usually 50 ml., for 1 hr. By "pure fat" is meant total non-volatile organic matter. The residual likuor was evaporated to dryness, and the residue was weighed before and after ignition—the difference representing pure fot not absorbed. The percentage, *A*, of the given fat that was absorbed was obtained by difference. Bound fat, *B*, was determined by extracting the fat-liquored Cr-tanned hide powder successively with H_2O, alcohol, petroleum ether, and ethyl ether, then hydrolyzing the leather with alcoholic KOH, removing alcohol by evaporation, boiling the hydrolyzate with HCl, and extracting with ethyl ether. *B* is figured as percentage of *A*. Variables studied were: quantity of fat given, volume of fat liquor, pH value of fat liquor, ratio of Cr to collagen in the tanned hide powder, basicity of the Cr alum used for tanning, extent of neutralization after tanning, and (for *B*) length of storage and tempreature of storage after fat-liquoring. In a general way, all the replacement fats acted very much like the natural sulfated oils, so far as concerns *A*. Thus, under standard conditions (hide powder tanned with 1.5 per cent Cr_2O_3 in the form of 33 per cent basic chrome alum, not neutralized, fat liquored with 5 per cent pure fat in 50 ml. at pH about 5), *A* was 95-96 per cent for Nos. 12 and 13, and 92-98 for all the replacement fats except Nos. 10 and 11, for which *A* was 78 and 75 respectively. *A* showed only minor and irregular fluctuation when the amount of fat given was halved or doubled. When the volume of fat liquor (with constant total fat) was doubled and quadrupled, *A* declined somewhat with increasing dilution, and the decrease in *A* with increasing dilution was greatest for those compounds giving lowest values for *A* under standard conditions. Only small and irregular differences in *A* resulted from varying the basicity of the chrome tan liquor from 0 to 50 per cent. *A* declined with increasing neutralization of the tanned powder (0,2,4 and 8 per cent borax), but this effect was marked only in going from 4 to 8 per cent borax. Reducing the amount of Cr_2O_3 given from 1.5 to 0.5 per cent had very little effect on *A*, but for untanned hide powder *A* was considerable lower (50-83) for all compounds except No. 5, No. 7, No. 9, and Nos. 12 and 13, for which *A* was 90 or above. Raising the pH value of the fatliquor from 5 to 7 and 9 reduced *A* slightly, except for Nos. 3, 5, 6, 8, 9, 12 and 13, for which *A* was unaffected or even increased slightly. The bound fat *(B)* varied greatly with the material. For Nos. 12 and 13, under standard conditions, *B* was 20-22 per cent of *A*. *B* was 2-8 per cent for Nos. 7, 8 and 9, which are high in unsaponifiable mineral oil, and 34 to 50 per cent for Nos. 1, 6, 10 and 11, all of which contain sulfo-acids that possess tanning properties. For Nos. 2-5, *B* was about the same as for the natural sulfated oils. In general those variables that brought about a decrease in *A* caused an increase in *B*, indicating preferential take-up of the components contributing to *B*. For most compounds, *B* increased with time of aging (at 20°C.) up to 30 days, but *B* decreased on aging for Nos. 2, 3, 4 and 5. Increasing the temperature from 20 to 60° during 2-day aging resulted in a barely perceptible increase in *B*. H. B. M.

Tannage with Economy of Chrome. By Hans Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 2, 73 (1949). The object of this work was to reduce the amount of chrome given without reducing the amount fixed—that is, to secure better utilization of chrome. In normal chrome tanning, the utilization of Cr_2O_3 given generally is only 70 per cent, and frequently only 50 to 60 per cent. Laboratory tannages were performed on bated calf skin, pickled with NaCl + HCl and tanned with a 33 per cent basic commercial chrome compound to give 2.5, 1.75, or 1.0 per cent Cr_2O_3 in the white weight, with the addition of one of the following auxiliary materials: 1. *Blancorol A*, containing 30-32 per cent Al_2O_3, basicity 40-45 per cent; used 2 per cent with 1.75 per cent Cr_2O_3 and 4 per cent with 1.0 per cent Cr_2O_3, neutralized with 0.3 and 0.6 per cent Na_2CO_3 respectively before adding to

the drum, added 2 hours after the chrome liquor. 2. *Blancorol B*, containing 40-42 per cent Al_2O_3, basicity about 70; used 1.5 per cent with 1.75 per cent Cr_2O_3 and 3.0 per cent with 1.0 per cent Cr_2O_3; not neutralized before addition; added 2 hours after the chrome liquor. 3. *Koreon P*, apparently an aluminum compound, composition not stated; used 5 per cent with 1.75 per cent Cr_2O_3 and 7 per cent with 1.0 per cent Cr_2O_3; not neutralized before addition; added 5 hours after chrome liquor. 4. *Novaltan CA*, another aluminum compound; used 2 per cent with 1.75 per cent Cr_2O_3 and 3 per cent with 1.0 per cent Cr_2O_3; mixed with chrome liquor before addition. 5. *Coriagen N*, a polymeric phosphate apparently similar to Calgon; used 1 per cent with 1 per cent Cr alum (0.15 per cent Cr_2O_3) as an overnight pickle, followed by adjustment of pH value to 5.2 with formic acid; 1.6 or 0.85 per cent Cr_2O_3 given as regular chrome liquor, followed by an additional 1 per cent of Coriagen N. 6. *Lorikal*, a fat replacement for chamois tanning; 8 per cent used at the fatliquoring stage, after chrome tannage with 1.75 or 1.0 per cent Cr_2O_3; stock was pickled with Dirinal P; the treatment with Lorikal was followed by further treatment with Dirinal F + $Al_2(SO_4)_3$. No information is given as to composition of the Dirinals. 7. *Ferrigan P*, an iron tanning

No.	Additive	% Cr_2O_3 given	% of Cr_2O_3 utilized	% Cr_2O_3 in leather (14% H_2O)	% Cr_2O_3 in leather as percentage of No. 1	% Al_2O_3 in leather
1.	None	2.5	58	3.8	100	0.2
2.	None	1.75	72	3.4	89	0.3
3.	None	1.0	84	2.2	58	0.2
4.	Blankorol A-2%	1.75	83	4.0	105	1.2
5.	Blankorol A-4%	1.0	96	3.2	84	1.6
6.	Blankorol B-1. 5%	1.75	85	4.4	116	1.1
7.	Blankorol B-3%	1.0	98	3.4	89	1.5
8.	Koreon P-5%	1.75	79	3.6	95	0.7
9.	Koreon P-7%	1.0	90	3.0	79	0.5
10.	Novaltan CA-2%	1.75	77	3.5	92	0.9
11.	Novaltan CA-3%	1.0	88	2.7	71	0.8
12.	Coriagen N-1%	1.75	83	3.8	100	0.4
13.	Coriagen N-1%	1.0	95	3.1	82	0.5
14.	Dirinial—4.5% (as pickle)	1.75	74	3.5	92	0.4
15.	Dirinial P-1% Lorikal—8% $Al_2(SO_4)_3$—3%	1.75	74	3.6	95	1.6
16.	Dirinal P—1% Lorikal—12% $Al_2(SO_4)_3$—5%	1.0	89	3.4	74	1.8
17.	Ferrigan P—15%	none	—	—	—	Fe_2O_3 7.6
18.	Ferrigan P—30%	none	—	—	—	9.1

compound; used as straight tannage (no Cr), following normal pickle; 15 and 30 per cent used. In all tests, the liquors were sapped as usual by addition of Na_2CO_3, and the leathers were further neutralized and given a normal fatliquor. All the first 5 materials listed gave increased Cr utilization, as shown by the accompanying table. Their effectiveness decreased in the order: Blankorol B, Blankoral A, Coriagen N, Koreon P, Novaltan CA. The first three yielded leathers that were as good as the standard, when the amount of Cr given was reduced by 30 per cent. Dirinal P in the pickle did not cause improved utilization. The Lorikal-retanned leather was soft, suitable for clothing but not for box calf. The Ferrigan leathers resembled vegetable-tanned leather. Practical tanning tests, employing only 42 to 63 per cent of the normal amount of Cr, showed that acceptable leather could be produced with any of the first 5 materials, although the leathers were somewhat firmer and flatter than when the full amount of chrome was given. Results of the Ferrigan P tannage varied greatly from lot to lot. H. B. M.

Technical Analysis of Leather Greasing Materials. By F. Stather and R. Schubert. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 1, 84 (1949). Commercial mixtures now sold (in Germany) for fatliquoring, stuffing, or oiling leather are, frequently, very complex. Besides natural fats, such mixtures often contain mineral oil, tar oil distillation products, paraffin, waxes, ceresine, wool grease, synthetic fatty acids, and synthetic ether- or ester-like replacement fats that have little or no resemblance, chemically, to natural fats. Sulfated fats and oils may contain sulfonates of the higher alcohols, aromatic sulfo-acids, or aliphatic sulfonation products of the Mersol type. Identification of all the components in such mixtures seldom is possible. The following scheme of analysis has proved useful. First determine whether or not the material emulsifies readily in water at 50-60°C. For all materials, determine water by the toluene distillation method; ash; Fe in ash; unsaponifiable matter; pH value of a solution obtained by shaking the fat with 50 volumes of water, for 24 hours, at a temperature above the melting point; and difference figure (change in pH value on 10-fold dilution of the above solution). For non-emulsifiable fats, determine organic non-fatty material (matter insoluble on extraction with ether in a Soxhlet apparatus, minus mineral matter), and acid number. For emulsifiable fats, determine total fatty acids, and sulfonation intensity. The latter is the ratio of combined acid sulfate to total fat (100 – per cent H_2O – per cent mineral matter). H. B. M.

Quality Standards for Vegetable Tanned Leathers. By F. Stather and R. Lauffmann. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 1, 50 (1949). Mineral and combination-tanned leathers. *ibid.* No. 2, 3 (1949). Analytical and physical test data are tabulated for about 2800 samples of all varieties of leather, examined at the Freiberg institute in 1943-5. For each kind of leather the results are broken down to show many samples gave results that fall within various limits, for each constituent or property The suggested standards are tabulated. The chemical data is for leathers containing 14 per cent water

See following tables. H. B. M.

VEGETABLE TANNED LEATHER

	SOLE	INSOLE	COWHIDE UPPER	PIG UPPER	CASE	UPHOLSTERY	BELTING	HARNESS	LINING (cattle, colt, goat pig)	LINING (sheep, lamb, rabbit)
Petroleum ether extract -%	not over 2.0		17–23		5–12	4–9	cold stuffed up to 12; warm stuffed up to 18; burned in up to 25	10–25		3–8
Ash -% (maximum)	old pit tannage 1.0 modern tannage 2.5 $MgSO_4/7H_2O$, 40.		1.0			2.0	1.0		2.0	
Water solubles -% (maximum)	organic: old pit tannage, 9.0; accelerated pit tannage, 12.0; modern tannage, 16.0; insoles, total 10.		Total water solubles, 6.0							
Degree of tannage	60–95		50–75			50–75			not under 50	
Acidity	Free strong acids absent; pH not under 3.5; difference figure not over 0.7 when pH value is below 4.5									
Density (g/cm³).	not over 1.0		——	——	——	——	——	——	——	——
Tensile strength (kg./cm².) (minimum)	225		250	200	250 (except 225 for pig)	150 (over 1.25 mm.) 100 (under 1.25 mm.)	250	250	250	100
% Stretch at break (maximum)	25		70			50				60
Stitch tear (kg./cm.) (minimum)	——	——	100	75	100 (except 75 for pig)	10 (over 1.25 min.) 30 (under 1.25 min.)	100		60	50
Tongue tear (kg./cm.) (minimum)	——	——	40	20	40 (except 20 for pig)	20 (over 1.25 min.) 15 (under 1.25 min.)	40		20	10

VEGETABLE TANNED LEATHER

		SOLE	INSOLE	COWHIDE UPPER	PIG UPPER	CASE	UP-HOLSTERY	BELTING	HARNESS	LINING (cattle, colt, goat pig)	LINING (sheep, lamb, rabbit)
% Water uptake (Kubelka)	2 hrs.	40 (max.)	25 (min.)	35 (max.)	60 (max.)	—	—	—	—	75 (min.)	
	24 hrs.	50 (max.)		45 (max.)	70 (max.)	—	—	—	—	100 (min.)	
Water Transmission quotient (Stather-Herfeld) (minimum)		old pit tannage 0.35; otherwise 0.60	—	0.25	much poorer than bovine upper leather	—	—	—	—	—	—
Air Transmission coefficient (Bergmann) (minimum)		20		80		—	—	—	—		250
Water vapor transmission no. (Herfeld) (minimum)		200	250	200							300
Wear coefficient (Stather-Herfeld) (maximum)		2.5	—	—	—	—	—	—	—	—	—

CHROME LEATHERS

	SOLE	UPPER (Calf or Cowhide)	WATERPROOF LEATHER (Cr. or Comb. tan)	PIG UPPER		BELTING	CLOTHING LEATHER goat, calf, young cows)	GLOVE	
				low fat	high fat			Cr Tan (calf, goat pig)	Al Tan
Petroleum ether extract – %	20–30 (Total impregnants)	2–6	17–23	4–8	17–23	cold stuffed up to 12; warm stuffed up to 17, burned in, up to 25.	4–10	not over 10	
Mineral matter (excluding Cr_2O_3 or Al_2O_3) – % (maximum)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	8.0
Cr_2O_3 – % (minimum)	2.5	2.5	straight Cr, 2.5; Comb. 1.5	2.5	2.5	2.5	2.5	2.0	2.0 (Al_2O_3)
Water Solubles – %		6.0 (Max.) (Comb.)							
Acidity	pH value not under 3.5; difference figure under 0.7 if pH is below 4.5								
Tensile Strength (kg./cm².) (minimum)	300	250	300	250	250	300	250	200	100
Strength at break, % (maximum)	60	75	80	70	70	75	60	50 (minimum)	
Stitch Tear (kg./cm.) (minimum)	——	100	120	80	80	120	60	60	40
Tongue Tear (kg. /cm.) (minimum)	——	40	60	25	25	50	25	25	15
% Water Uptake (Kubelka) (maximum) 2 hrs.	10	60	30	75	60	——	——	——	——
24 hrs.	20	85	45	100	75	——	——	——	——
Water Transmission Quotient (Stather-Herfeld) (minimum)	0.70	0.50	0.80	Generally much poorer than for cattlehide upper		——	0.60	——	——
Air Transmission Coefficient (Bergmann) (minimum)	Generally impermeable	80	a certain permeability is desirable	80	80	——	75	——	——
Water Vapor Transmission No. (Herfeld) (minimum)	50	250	175	250	250	——	250	——	——
Wear Coefficient (Stather-Herfeld) (maximum)	1.0	——	——	——	——	——	——	——	——

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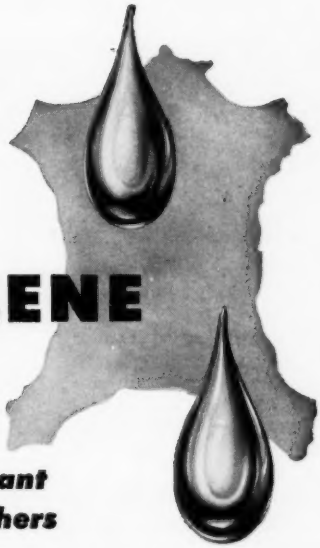

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INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY V
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXV
ARKANSAS COMPANY, INC. VI
ARTHUR C. TRASK CO. XXXIV
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARKEY IMPORTING CO., INC. XXXII
BARIUM REDUCTION CORPORATION XXXI
BONA ALLEN, INC. XXVIII
BUCKMAN LABORATORIES, INC. XVIII
CALCO CHEMICAL DIV. XIX
CHEMTAN COMPANY XXI
E. F. DREW & CO., INC. XXIX
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXIV
GARDEN STATE TANNING INC. XXXVII
GEIGY COMPANY, INC. XXXIII
GARVAMNES AB WEIBULL XXXIX
GENERAL DYESTUFF CORPORATION IX
HOOKER ELECTROCHEMICAL CO. XVII
HOWES LEATHER CO., INC. XXVIII
INTERNATIONAL PRODUCTS CORP. XII
KEI'EC CHEMICAL CORPORATION XXXIV
LEATHER AND SHOES XXXVI
LEATHER MANUFACTURER, THE XXXV
L. H. LINCOLN & SON, INC. XL
MARDEN WILD CORPORATION XXVI
MARTIN DENNIS CO., THE VII
MEAD CORPORATION, THE XIII
MUTUAL CHEMICAL CO. OF AMERICA XXXVIII
NATIONAL ANALINE DIVISION, ALLIED CHEMICAL & DYE CORP. IV
NEWARK LEATHER FINISH CO. XXXV
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXXVII
REILLY-WHITEMAN-WALTON CO. XXXVII
RIVER PLATE IMPORT AND EXPORT CORPORATION, THE XX
ROBESON PROCESS CO. II
ROHM & HAAS XV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SANDOZ CHEMICAL WORKS, INC. XIV
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XLII—Inside Back Cover
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXVII—XL
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXV
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXXIV
WOLF, JACQUES & CO. VIII

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INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
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